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## Sample Exercise 16.1 Identifying Conjugate Acids and Bases

(a) What is the conjugate base of each of the following acids:  $\text{HClO}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_4^+$ ,  $\text{HCO}_3^-$ ? (b) What is the conjugate acid of each of the following bases:  $\text{CN}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ?

### Solution

**Analyze:** We are asked to give the conjugate base for each of a series of species and to give the conjugate acid for each of another series of species.

**Plan:** The conjugate base of a substance is simply the parent substance minus one proton, and the conjugate acid of a substance is the parent substance plus one proton.

**Solve:** (a)  $\text{HClO}_4$  less one proton ( $\text{H}^+$ ) is  $\text{ClO}_4^-$ . The other conjugate bases are  $\text{HS}^-$ ,  $\text{PH}_3$ , and  $\text{CO}_3^{2-}$ . (b)  $\text{CN}^-$  plus one proton ( $\text{H}^+$ ) is  $\text{HCN}$ . The other conjugate acids are  $\text{HSO}_4^-$ ,  $\text{H}_3\text{O}^+$ , and  $\text{H}_2\text{CO}_3$ .

Notice that the hydrogen carbonate ion ( $\text{HCO}_3^-$ ) is amphiprotic. It can act as either an acid or a base.

### Practice Exercise

Write the formula for the conjugate acid of each of the following:  $\text{HSO}_3^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}$ .

**Answers:**  $\text{H}_2\text{SO}_3$ ,  $\text{HF}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HCO}^+$

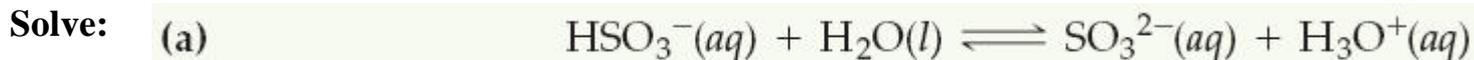
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## Sample Exercise 16.2 Writing Equations for Proton-Transfer Reactions

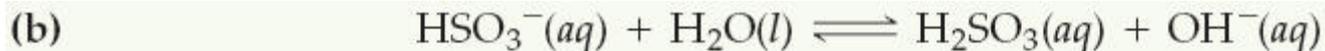
The hydrogen sulfite ion ( $\text{HSO}_3^-$ ) is amphiprotic. **(a)** Write an equation for the reaction of  $\text{HSO}_3^-$  with water, in which the ion acts as an acid. **(b)** Write an equation for the reaction of  $\text{HSO}_3^-$  with water, in which the ion acts as a base. In both cases identify the conjugate acid–base pairs.

### Solution

**Analyze and Plan:** We are asked to write two equations representing reactions between  $\text{HSO}_3^-$  and water, one in which  $\text{HSO}_3^-$  should donate a proton to water, thereby acting as a Brønsted–Lowry acid, and one in which  $\text{HSO}_3^-$  should accept a proton from water, thereby acting as a base. We are also asked to identify the conjugate pairs in each equation.



The conjugate pairs in this equation are  $\text{HSO}_3^-$  (acid) and  $\text{SO}_3^{2-}$  (conjugate base); and  $\text{H}_2\text{O}$  (base) and  $\text{H}_3\text{O}^+$  (conjugate acid).



The conjugate pairs in this equation are  $\text{H}_2\text{O}$  (acid) and  $\text{OH}^-$  (conjugate base), and  $\text{HSO}_3^-$  (base) and  $\text{H}_2\text{SO}_3$  (conjugate acid).

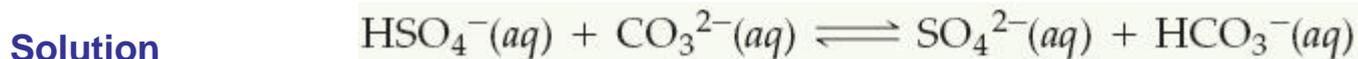
### Practice Exercise

When lithium oxide ( $\text{Li}_2\text{O}$ ) is dissolved in water, the solution turns basic from the reaction of the oxide ion ( $\text{O}_2^-$ ) with water. Write the reaction that occurs, and identify the conjugate acid–base pairs.

**Answer:**  $\text{O}^{2-}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{OH}^-(aq) + \text{OH}^-(aq)$ .  $\text{OH}^-$  is the conjugate acid of the base  $\text{O}^{2-}$ .  $\text{OH}^-$  is also the conjugate base of the acid  $\text{H}_2\text{O}$ .

## Sample Exercise 16.3 Predicting the Position of a Proton-Transfer Equilibrium

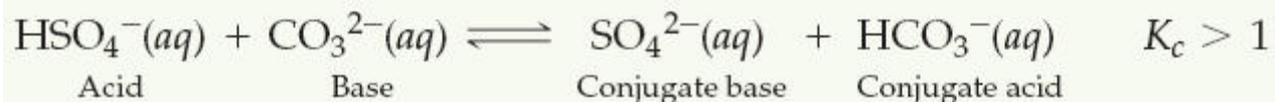
For the following proton-transfer reaction, use Figure 16.4 to predict whether the equilibrium lies predominantly to the left (that is,  $K_c < 1$ ) or to the right ( $K_c > 1$ ):



**Analyze:** We are asked to predict whether the equilibrium shown lies to the right, favoring products, or to the left, favoring reactants.

**Plan:** This is a proton-transfer reaction, and the position of the equilibrium will favor the proton going to the stronger of two bases. The two bases in the equation are  $\text{CO}_3^{2-}$ , the base in the forward reaction as written, and  $\text{SO}_4^{2-}$  the conjugate base of  $\text{HSO}_4^-$ . We can find the relative positions of these two bases in Figure 16.4 to determine which is the stronger base.

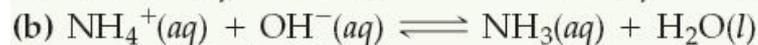
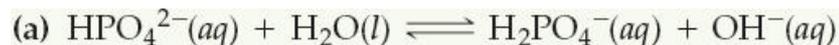
**Solve:**  $\text{CO}_3^{2-}$  appears lower in the right-hand column in Figure 16.4 and is therefore a stronger base than  $\text{SO}_4^{2-}$ .  $\text{CO}_3^{2-}$ , therefore, will get the proton preferentially to become  $\text{HCO}_3^-$ , while  $\text{SO}_4^{2-}$  will remain mostly unprotonated. The resulting equilibrium will lie to the right, favoring products (that is,  $K_c > 1$ ).



**Comment:** Of the two acids in the equation,  $\text{HSO}_4^-$  and  $\text{HCO}_3^-$ , the stronger one gives up a proton more readily while the weaker one tends to retain its proton. Thus, the equilibrium favors the direction in which the proton moves from the stronger acid and becomes bonded to the stronger base.

### Practice Exercise

For each of the following reactions, use Figure 16.4 to predict whether the equilibrium lies predominantly to the left or to the right:



**Answers:** (a) left, (b) right

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## Sample Exercise 16.4 Calculating $[H^+]$ for Pure Water

Calculate the values of  $[H^+]$  and  $[OH^-]$  in a neutral solution at 25 °C.

### Solution

**Analyze:** We are asked to determine the concentrations of  $H^+$  and  $OH^-$  ions in a neutral solution at 25 °C.

**Plan:** We will use Equation 16.16 and the fact that, by definition,  $[H^+] = [OH^-]$  in a neutral solution.

**Solve:** We will represent the concentration of  $[H^+]$  and  $[OH^-]$  in neutral solution with  $x$ . This gives

$$\begin{aligned} [H^+][OH^-] &= (x)(x) = 1.0 \times 10^{-14} \\ x^2 &= 1.0 \times 10^{-14} \\ x &= 1.0 \times 10^{-7} M = [H^+] = [OH^-] \end{aligned}$$

In an acid solution  $[H^+]$  is greater than  $1.0 \times 10^{-7} M$  in a basic solution  $[H^+]$  is less than  $1.0 \times 10^{-7} M$ .

### Practice Exercise

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:

(a)  $[H^+] = 4 \times 10^{-9} M$ ; (b)  $[H^+] = 4 \times 10^{-9} M$ ; (c)  $[OH^-] = 7 \times 10^{-13} M$ .

**Answers:** (a) basic, (b) neutral, (c) acidic

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## Sample Exercise 16.5 Calculating $[H^+]$ from $[OH^-]$

Calculate the concentration of  $H^+(aq)$  in (a) a solution in which  $[OH^-]$  is  $0.010 M$ , (b) a solution in which  $[OH^-]$  is  $1.8 \times 10^{-9} M$ .

*Note:* In this problem and all that follow, we assume, unless stated otherwise, that the temperature is  $25^\circ C$ .

### Solution

**Analyze:** We are asked to calculate the hydronium ion concentration in an aqueous solution where the hydroxide concentration is known.

**Plan:** We can use the equilibrium-constant expression for the autoionization of water and the value of  $K_w$  to solve for each unknown concentration.

### Solve:

a) Using Equation 16.16, we have:

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

This solution is basic because

$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12} M$$

$$[OH^-] > [H^+]$$

(b) In this instance

This solution is acidic because

$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6} M$$

$$[H^+] > [OH^-]$$

### Practice Exercise

Calculate the concentration of  $OH^-(aq)$  in a solution in which (a)  $[H^+] = 2 \times 10^{-6} M$ ; (b)  $[H^+] = [OH^-]$ ; (c)  $[H^+] = 100 \times [OH^-]$ .

**Answers:** (a)  $5 \times 10^{-9} M$ , (b)  $1.0 \times 10^{-7} M$ , (c)  $1.0 \times 10^{-8} M$

## Sample Exercise 16.6 Calculating pH from $[H^+]$

Calculate the pH values for the two solutions described in Sample Exercise 16.5.

### Solution

**Analyze:** We are asked to determine the pH of aqueous solutions for which we have already calculated  $[H^+]$ .

**Plan:** We can calculate pH using its defining equation, Equation 16.17.

**Solve:**

(a) In the first instance we found  $[H^+]$  to be  $1.0 \times 10^{-12} M$ .

$$\text{pH} = -\log(1.0 \times 10^{-12}) = -(-12.00) = 12.00$$

Because  $1.0 \times 10^{-12}$  has two significant figures, the pH has two decimal places, 12.00. (b) For the second solution,  $[H^+] = 5.6 \times 10^{-6} M$ . Before performing the calculation, it is helpful to estimate the pH. To do so, we note that  $[H^+]$  lies between  $1 \times 10^{-6}$  and  $1 \times 10^{-5}$

$$1 \times 10^{-6} < 5.6 \times 10^{-6} < 1 \times 10^{-5}$$

Thus, we expect the pH to lie between 6.0 and 5.0. We use Equation 16.17 to calculate the pH.

$$\text{pH} = -\log(5.6 \times 10^{-6}) = 5.25$$

**Check:** After calculating a pH, it is useful to compare it to your prior estimate. In this case the pH, as we predicted, falls between 6 and 5. Had the calculated pH and the estimate not agreed, we should have reconsidered our calculation or estimate or both.

### Practice Exercise

(a) In a sample of lemon juice  $[H^+]$  is  $3.8 \times 10^{-4} M$ . What is the pH? (b) A commonly available window-cleaning solution has  $[OH^-] = 1.9 \times 10^{-6} M$ . What is the pH?

**Answers:** (a) 3.42, (b)  $[H^+] = 5.3 \times 10^{-9} M$ , so pH = 8.28

## Sample Exercise 16.7 Calculating $[H^+]$ from pH

A sample of freshly pressed apple juice has a pH of 3.76. Calculate  $[H^+]$ .

### Solution

**Analyze:** We need to calculate  $[H^+]$  from pH.

**Plan:** We will use Equation 16.17,  $pH = -\log[H^+]$ , for the calculation.

**Solve:** From Equation 16.17, we have

$$pH = -\log[H^+] = 3.76$$

Thus,

$$\log[H^+] = -3.76$$

To find  $[H^+]$ , we need to determine the *antilog* of  $-3.76$ . Scientific calculators have an antilog function (sometimes labeled INV log or  $10^x$ ) that allows us to perform the calculation:

$$[H^+] = \text{antilog}(-3.76) = 10^{-3.76} = 1.7 \times 10^{-4} M$$

**Comment:** Consult the user's manual for your calculator to find out how to perform the antilog operation. The number of significant figures in  $[H^+]$  is two because the number of decimal places in the pH is two.

**Check:** Because the pH is between 3.0 and 4.0, we know that  $[H^+]$  will be between  $1 \times 10^{-3}$  and  $1 \times 10^{-4} M$ . Our calculated  $[H^+]$  falls within this estimated range.

### Practice Exercise

A solution formed by dissolving an antacid tablet has a pH of 9.18. Calculate  $[H^+]$ .

**Answer:**  $[H^+] = 6.6 \times 10^{-10} M$

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## Sample Exercise 16.8 Calculating the pH of a Strong Acid

What is the pH of a 0.040 *M* solution of HClO<sub>4</sub>?

### Solution

**Analyze and Plan:** Because HClO<sub>4</sub> is a strong acid, it is completely ionized, giving [H<sup>+</sup>] = [ClO<sub>4</sub><sup>-</sup>] = 0.040 *M*

**Solve:** The pH of the solution is given by

$$\text{pH} = -\log(0.040) = 1.40.$$

**Check:** Because [H<sup>+</sup>] lies between  $1 \times 10^{-2}$  and  $1 \times 10^{-1}$ , the pH will be between 2.0 and 1.0. Our calculated pH falls within the estimated range. Furthermore, because the concentration has two significant figures, the pH has two decimal places.

### Practice Exercise

An aqueous solution of HNO<sub>3</sub> has a pH of 2.34. What is the concentration of the acid?

**Answer:** 0.0046 *M*

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## Sample Exercise 16.9 Calculating the pH of a Strong Base

What is the pH of (a) a 0.028 M solution of NaOH, (b) a 0.0011 M solution of Ca(OH)<sub>2</sub>?

### Solution

**Analyze:** We are asked to calculate the pH of two solutions of strong bases.

**Plan:** We can calculate each pH by either of two equivalent methods. First, we could use Equation 16.16 to calculate [H<sup>+</sup>] and then use Equation 16.17 to calculate the pH. Alternatively, we could use [OH<sup>-</sup>] to calculate pOH and then use Equation 16.20 to calculate the pH.

### Solve:

(a) NaOH dissociates in water to give one OH<sup>-</sup> ion per formula unit. Therefore, the OH<sup>-</sup> concentration for the solution in (a) equals the stated concentration of NaOH, namely 0.028 M.

*Method 1:*

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.028} = 3.57 \times 10^{-13} \text{ M} \quad \text{pH} = -\log(3.57 \times 10^{-13}) = 12.45$$

*Method 2:*

$$\text{pOH} = -\log(0.028) = 1.55 \quad \text{pH} = 14.00 - \text{pOH} = 12.45$$

(b) Ca(OH)<sub>2</sub> is a strong base that dissociates in water to give two OH<sup>-</sup> ions per formula unit. Thus, the concentration of OH<sup>-</sup>(aq) for the solution in part (b) is 2 × (0.0011 M) = 0.0022 M

*Method 1:*

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.0022} = 4.55 \times 10^{-12} \text{ M} \quad \text{pH} = -\log(4.55 \times 10^{-12}) = 11.34$$

*Method 2:*

$$\text{pOH} = -\log(0.0022) = 2.66 \quad \text{pH} = 14.00 - \text{pOH} = 11.34$$

### Practice Exercise

What is the concentration of a solution of (a) KOH for which the pH is 11.89; (b) Ca(OH)<sub>2</sub> for which the pH is 11.68?

**Answers:** (a)  $7.8 \times 10^{-3} \text{ M}$ , (b)  $2.4 \times 10^{-3} \text{ M}$

## Sample Exercise 16.10 Calculating $K_a$ from Measured pH

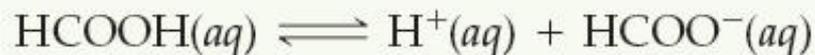
A student prepared a 0.10  $M$  solution of formic acid ( $\text{HCOOH}$ ) and measured its pH. The pH at 25 °C was found to be 2.38. Calculate  $K_a$  for formic acid at this temperature.

### Solution

**Analyze:** We are given the molar concentration of an aqueous solution of weak acid and the pH of the solution, and we are asked to determine the value of  $K_a$  for the acid.

**Plan:** Although we are dealing specifically with the ionization of a weak acid, this problem is very similar to the equilibrium problems we encountered in Chapter 15. We can solve this problem using the method first outlined in Sample Exercise 15.9, starting with the chemical reaction and a tabulation of initial and equilibrium concentrations.

**Solve:** The first step in solving any equilibrium problem is to write the equation for the equilibrium reaction. The ionization of formic acid can be written as follows:



The equilibrium-constant expression is

From the measured pH, we can calculate  $[\text{H}^+]$ :

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

We can do a little accounting to determine the concentrations of the species involved in the equilibrium. We imagine that the solution is initially 0.10  $M$  in  $\text{HCOOH}$  molecules. We then consider the ionization of the acid into  $\text{H}^+$  and  $\text{HCOO}^-$ . For each  $\text{HCOOH}$  molecule that ionizes, one  $\text{H}^+$  ion and one ion  $\text{HCOO}^-$  are produced in solution. Because the pH measurement indicates that  $[\text{H}^+] = 4.2 \times 10^{-3} M$  at equilibrium, we can construct the following table:

$$\text{pH} = -\log[\text{H}^+] = 2.38$$

$$\log[\text{H}^+] = -2.38$$

$$[\text{H}^+] = 10^{-2.38} = 4.2 \times 10^{-3} M$$

## Sample Exercise 16.10 Calculating $K_a$ from Measured pH

### Solution (Continued)

Notice that we have neglected the very small concentration of  $\text{H}^+(\text{aq})$  that is due to the autoionization of  $\text{H}_2\text{O}$ . Notice also that the amount of  $\text{HCOOH}$  that ionizes is very small compared with the initial concentration of the acid. To the number of significant figures we are using, the subtraction yields  $0.10\text{ M}$ :

	$\text{HCOOH}(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	+	$\text{HCOO}^-(\text{aq})$
Initial	$0.10\text{ M}$		$0$		$0$
Change	$-4.2 \times 10^{-3}\text{ M}$		$+4.2 \times 10^{-3}\text{ M}$		$+4.2 \times 10^{-3}\text{ M}$
Equilibrium	$(0.10 - 4.2 \times 10^{-3})\text{ M}$		$4.2 \times 10^{-3}\text{ M}$		$4.2 \times 10^{-3}\text{ M}$

$$(0.10 - 4.2 \times 10^{-3})\text{ M} \approx 0.10\text{ M}$$

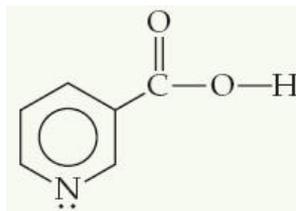
We can now insert the equilibrium concentrations into the expression for  $K_a$ :

$$K_a = \frac{(4.2 \times 10^{-3})(4.2 \times 10^{-3})}{0.10} = 1.8 \times 10^{-4}$$

**Check:** The magnitude of our answer is reasonable because  $K_a$  for a weak acid is usually between  $10^{-3}$  and  $10^{-10}$

### Practice Exercise

Niacin, one of the B vitamins, has the following molecular structure:



A  $0.020\text{ M}$  solution of niacin has a pH of 3.26. What is the acid-dissociation constant,  $K_a$ , for niacin?

**Answers:**  $1.5 \times 10^{-5}$

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## Sample Exercise 16.11 Calculating Percent Ionization

A 0.10 M solution of formic acid (HCOOH) contains  $4.2 \times 10^{-3} M$   $H^+(aq)$ . Calculate the percentage of the acid that is ionized.

### Solution

**Analyze:** We are given the molar concentration of an aqueous solution of weak acid and the equilibrium concentration of  $H^+(aq)$  and asked to determine the percent ionization of the acid.

**Plan:** The percent ionization is given by Equation 16.27.

**Solve:**

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HCOOH]_{\text{initial}}} \times 100\% = \frac{4.2 \times 10^{-3} M}{0.10 M} \times 100\% = 4.2\%$$

### Practice Exercise

A 0.020 M solution of niacin has a pH of 3.26. Calculate the percent ionization of the niacin.

**Answer:** 2.7%

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## Sample Exercise 16.12 Using $K_a$ to Calculate pH

Calculate the pH of a 0.20 M solution of HCN. (Refer to Table 16.2 or Appendix D for the value of  $K_a$ .)

### Solution

**Analyze:** We are given the molarity of a weak acid and are asked for the pH. From Table 16.2,  $K_a$  for HCN is  $4.9 \times 10^{-10}$ .

**Plan:** We proceed as in the example just worked in the text, writing the chemical equation and constructing a table of initial and equilibrium concentrations in which the equilibrium concentration of  $H^+$  is our unknown.

**Solve:** Writing both the chemical equation for the ionization reaction that forms  $H^+(aq)$  and the equilibrium-constant ( $K_a$ ) expression for the reaction:



$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = 4.9 \times 10^{-10}$$

Next, we tabulate the concentration of the species involved in the equilibrium reaction, letting  $x = [H^+]$  at equilibrium:

	$\text{HCN}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CN}^-(aq)$
Initial	0.20 M		0		0
Change	$-x$ M		$+x$ M		$+x$ M
Equilibrium	$(0.20 - x)$ M		$x$ M		$x$ M

Substituting the equilibrium concentrations from the table into the equilibrium-constant expression yields

$$K_a = \frac{(x)(x)}{0.20 - x} = 4.9 \times 10^{-10}$$

## Sample Exercise 16.12 Using $K_a$ to Calculate pH

### Solution (Continued)

We next make the simplifying approximation that  $x$ , the amount of acid that dissociates, is small compared with the initial concentration of acid; that is,

Thus,

Solving for  $x$ , we have

A concentration of  $9.9 \times 10^{-6} M$  is much smaller than 5% of 0.20, the initial HCN concentration. Our simplifying approximation is therefore appropriate. We now calculate the pH of the solution:

$$0.20 - x \simeq 0.20$$

$$\frac{x^2}{0.20} = 4.9 \times 10^{-10}$$

$$x^2 = (0.20)(4.9 \times 10^{-10}) = 0.98 \times 10^{-10}$$

$$x = \sqrt{0.98 \times 10^{-10}} = 9.9 \times 10^{-6} M = [H^+]$$

$$\text{pH} = -\log[H^+] = -\log(9.9 \times 10^{-6}) = 5.00$$

### Practice Exercise

The  $K_a$  for niacin (Practice Exercise 16.10) is  $1.5 \times 10^{-5}$ . What is the pH of a 0.010  $M$  solution of niacin?

**Answer:** 3.41

## Sample Exercise 16.13 Using $K_a$ to Calculate Percent Ionization

Calculate the percentage of HF molecules ionized in (a) a 0.10 M HF solution, (b) a 0.010 M HF solution.

### Solution

**Analyze:** We are asked to calculate the percent ionization of two HF solutions of different concentration. From Appendix D, we find  $K_a = 6.8 \times 10^{-4}$ .

**Plan:** We approach this problem as we would previous equilibrium problems. We begin by writing the chemical equation for the equilibrium and tabulating the known and unknown concentrations of all species. We then substitute the equilibrium concentrations into the equilibrium-constant expression and solve for the unknown concentration, that of  $H^+$ .

### Solve:

(a) The equilibrium reaction and equilibrium concentrations are as follows:

	HF(aq)	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{F}^-(aq)$
Initial	0.10 M		0		0
Change	$-x$ M		$+x$ M		$+x$ M
Equilibrium	$(0.10 - x)$ M		$x$ M		$x$ M

The equilibrium-constant expression is

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{0.10 - x} = 6.8 \times 10^{-4}$$

When we try solving this equation using the approximation  $0.10 - x = 0.10$  (that is, by neglecting the concentration of acid that ionizes in comparison with the initial concentration), we obtain

$$x = 8.2 \times 10^{-3} \text{ M}$$

## Sample Exercise 16.13 Using $K_a$ to Calculate Percent Ionization

### Solution (Continued)

Because this value is greater than 5% of 0.10 M, we should work the problem without the approximation, using an equation-solving calculator or the quadratic formula. Rearranging our equation and writing it in standard quadratic form, we have

This equation can be solved using the standard quadratic formula.

Substituting the appropriate numbers gives

Of the two solutions, only the one that gives a positive value for  $x$  is chemically reasonable. Thus,

From our result, we can calculate the percent of molecules ionized:

**(b)** Proceeding similarly for the 0.010 M solution, we have

Solving the resultant quadratic expression, we obtain

The percentage of molecules ionized is

$$\begin{aligned}x^2 &= (0.10 - x)(6.8 \times 10^{-4}) \\ &= 6.8 \times 10^{-5} - (6.8 \times 10^{-4})x \\ x^2 + (6.8 \times 10^{-4})x - 6.8 \times 10^{-5} &= 0\end{aligned}$$

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

$$\begin{aligned}x &= \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 + 4(6.8 \times 10^{-5})}}{2} \\ &= \frac{-6.8 \times 10^{-4} \pm 1.6 \times 10^{-2}}{2}\end{aligned}$$

$$x = [\text{H}^+] = [\text{F}^-] = 7.9 \times 10^{-3} \text{ M}$$

$$\begin{aligned}\text{Percent ionization of HF} &= \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\% \\ &= \frac{7.9 \times 10^{-3} \text{ M}}{0.10 \text{ M}} \times 100\% = 7.9\%\end{aligned}$$

$$\frac{x^2}{0.010 - x} = 6.8 \times 10^{-4}$$

$$x = [\text{H}^+] = [\text{F}^-] = 2.3 \times 10^{-3} \text{ M}$$

$$\frac{0.0023 \text{ M}}{0.010 \text{ M}} \times 100\% = 23\%$$

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## Sample Exercise 16.13 Using $K_a$ to Calculate Percent Ionization

### Solution (Continued)

**Comment:** Notice that if we do not use the quadratic formula to solve the problem properly, we calculate 8.2% ionization for (a) and 26% ionization for (b). Notice also that in diluting the solution by a factor of 10, the percentage of molecules ionized increases by a factor of 3. This result is in accord with what we see in Figure 16.9. It is also what we would expect from Le Châtelier's principle. (Section 15.7) There are more "particles" or reaction components on the right side of the equation than on the left. Dilution causes the reaction to shift in the direction of the larger number of particles because this counters the effect of the decreasing concentration of particles.

### Practice Exercise

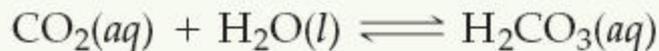
In Practice Exercise 16.11, we found that the percent ionization of niacin ( $K_a = 1.5 \times 10^{-5}$ ) in a 0.020  $M$  solution is 2.7%. Calculate the percentage of niacin molecules ionized in a solution that is (a) 0.010  $M$ , (b)  $1.0 \times 10^{-3} M$ .

**Answers:** (a) 3.9%, (b) 12%

---

## Sample Exercise 16.14 Calculating the pH of a Polyprotic Acid Solution

The solubility of  $\text{CO}_2$  in pure water at  $25^\circ\text{C}$  and  $0.1\text{ atm}$  pressure is  $0.0037\text{ M}$ . The common practice is to assume that all of the dissolved  $\text{CO}_2$  is in the form of carbonic acid ( $\text{H}_2\text{CO}_3$ ), which is produced by reaction between the  $\text{CO}_2$  and  $\text{H}_2\text{O}$ :



What is the pH of a  $0.0037\text{ M}$  solution of  $\text{H}_2\text{CO}_3$ ?

### Solution

**Analyze:** We are asked to determine the pH of a  $0.0037\text{ M}$  solution of a polyprotic acid.

**Plan:**  $\text{H}_2\text{CO}_3$  is a diprotic acid; the two acid-dissociation constants,  $K_{a1}$  and  $K_{a2}$  (Table 16.3), differ by more than a factor of  $10_3$ . Consequently, the pH can be determined by considering only  $K_{a1}$ , thereby treating the acid as if it were a monoprotic acid.

**Solve:** Proceeding as in Sample Exercises 16.12 and 16.13, we can write the equilibrium reaction and equilibrium concentrations as follows:

The equilibrium-constant expression is as follows:

Solving this equation using an equation-solving calculator, we get

Alternatively, because  $K_{a1}$  is small, we can make the simplifying approximation that  $x$  is small, so that

	$\text{H}_2\text{CO}_3(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	+	$\text{HCO}_3^-(\text{aq})$
Initial	$0.0037\text{ M}$		0		0
Change	$-x\text{ M}$		$+x\text{ M}$		$+x\text{ M}$
Equilibrium	$(0.0037 - x)\text{ M}$		$x\text{ M}$		$x\text{ M}$

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{0.0037 - x} = 4.3 \times 10^{-7}$$

$$x = 4.0 \times 10^{-5}\text{ M}$$

$$0.0037 - x \approx 0.0037$$

$$\frac{(x)(x)}{0.0037} = 4.3 \times 10^{-7}$$

$$x^2 = (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9}$$

$$x = [\text{H}^+] = [\text{HCO}_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\text{ M}$$

## Sample Exercise 16.14 Calculating the pH of a Polyprotic Acid Solution

### Solution (Continued)

Thus,  
Solving for  $x$ , we have

The small value of  $x$  indicates that our simplifying assumption was justified. The pH is therefore

$$\text{pH} = -\log[\text{H}^+] = -\log(4.0 \times 10^{-5}) = 4.40$$

**Comment:** If we were asked to solve for  $[\text{CO}_3^{2-}]$ , we would need to use  $K_{a2}$ . Let's illustrate that calculation. Using the values of  $[\text{HCO}_3^-]$  and  $[\text{H}^+]$  calculated above, and setting  $[\text{CO}_3^{2-}] = y$ , we have the following initial and equilibrium concentration values:

Assuming that  $y$  is small compared to  $4.0 \times 10^{-5}$ , we have

	$\text{HCO}_3^-(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CO}_3^{2-}(aq)$
Initial	$4.0 \times 10^{-5} M$		$4.0 \times 10^{-5} M$		0
Change	$-y M$		$+y M$		$+y M$
Equilibrium	$(4.0 \times 10^{-5} - y) M$		$(4.0 \times 10^{-5} + y) M$		$y M$

$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$
$$y = 5.6 \times 10^{-11} M = [\text{CO}_3^{2-}]$$

The value calculated for  $y$  is indeed very small compared to  $4.0 \times 10^{-5}$ , showing that our assumption was justified. It also shows that the ionization of  $\text{HCO}_3^-$  is negligible compared to that of  $\text{H}_2\text{CO}_3$ , as far as production of  $\text{H}^+$  is concerned. However, it is the *only* source of  $\text{CO}_3^{2-}$ , which has a very low concentration in the solution. Our calculations thus tell us that in a solution of carbon dioxide in water, most of the  $\text{CO}_2$  is in the form of  $\text{CO}_2$  or  $\text{H}_2\text{CO}_3$ , a small fraction ionizes to form  $\text{H}^+$  and  $\text{HCO}_3^-$ , and an even smaller fraction ionizes to give  $\text{CO}_3^{2-}$ . Notice also that  $[\text{CO}_3^{2-}]$  is numerically equal to  $K_{a2}$ .

---

## Sample Exercise 16.14 Calculating the pH of a Polyprotic Acid Solution

### Practice Exercise

(a) Calculate the pH of a 0.020 M solution of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ). (See Table 16.3 for  $K_{a1}$  and  $K_{a2}$ .)

(b) Calculate the concentration of oxalate ion [ $\text{C}_2\text{O}_4^{2-}$ ], in this solution.

**Answers:** (a) pH = 1.80 , (b) [ $\text{C}_2\text{O}_4^{2-}$ ] =  $6.4 \times 10^{-5}$  M

---

## Sample Exercise 16.15 Using $K_b$ to Calculate $\text{OH}^-$

Calculate the concentration of  $\text{OH}^-$  in a 0.15 M solution of  $\text{NH}_3$ .

### Solution

**Analyze:** We are given the concentration of a weak base and are asked to determine the concentration of  $\text{OH}^-$ .

**Plan:** We will use essentially the same procedure here as used in solving problems involving the ionization of weak acids; that is, we write the chemical equation and tabulate initial and equilibrium concentrations.

**Solve:** We first write the ionization reaction and the corresponding equilibrium-constant ( $K_b$ ) expression:



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

We then tabulate the equilibrium concentrations involved in the equilibrium:

(We ignore the concentration of  $\text{H}_2\text{O}$  because it is not involved in the equilibrium-constant expression.) Inserting these quantities into the equilibrium-constant expression gives the following:

Because  $K_b$  is small, we can neglect the small amount of  $\text{NH}_3$  that reacts with water, as compared to the total  $\text{NH}_3$  concentration; that is, we can neglect  $x$  relative to 0.15 M. Then we have

	$\text{NH}_3(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{NH}_4^+(\text{aq})$	+	$\text{OH}^-(\text{aq})$
Initial	0.15 M		—		0		0
Change	$-x$ M		—		$+x$ M		$+x$ M
Equilibrium	$(0.15 - x)$ M		—		$x$ M		$x$ M

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)(x)}{0.15 - x} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.15} = 1.8 \times 10^{-5}$$

$$x^2 = (0.15)(1.8 \times 10^{-5}) = 2.7 \times 10^{-6}$$

$$x = [\text{NH}_4^+] = [\text{OH}^-] = \sqrt{2.7 \times 10^{-6}} = 1.6 \times 10^{-3} \text{ M}$$

---

## Sample Exercise 16.15 Using $K_b$ to Calculate $\text{OH}^-$

### Solution (Continued)

**Check:** The value obtained for  $x$  is only about 1% of the  $\text{NH}_3$  concentration, 0.15  $M$ . Therefore, neglecting  $x$  relative to 0.15 was justified.

**Comment:** You may be asked to find the pH of a solution of a weak base. Once you have found  $[\text{OH}^-]$ , you can proceed as in Sample Exercise 16.9, where we calculated the pH of a strong base. In the present sample exercise, we have seen that the 0.15  $M$  solution of  $\text{NH}_3$  contains  $[\text{OH}^-] = 1.6 \times 10^{-3} M$ . Thus,  $\text{pOH} = -\log(1.6 \times 10^{-3}) = 2.80$ , and  $\text{pH} = 14.00 - 2.80 = 11.20$ . The pH of the solution is above 7 because we are dealing with a solution of a base.

### Practice Exercise

Which of the following compounds should produce the highest pH as a 0.05  $M$  solution: pyridine, methylamine, or nitrous acid?

**Answer:** methylamine (because it has the largest  $K_b$  value of the two amine bases in the list)

---

## Sample Exercise 16.16 Using pH to Determine the Concentration of a Salt

A solution made by adding solid sodium hypochlorite (NaClO) to enough water to make 2.00 L of solution has a pH of 10.50. Using the information in Equation 16.37, calculate the number of moles of NaClO that were added to the water.

### Solution

**Analyze:** We are given the pH of a 2.00-L solution of NaClO and must calculate the number of moles of NaClO needed to raise the pH to 10.50. NaClO is an ionic compound consisting of  $\text{Na}^+$  and  $\text{ClO}^-$  ions. As such, it is a strong electrolyte that completely dissociates in solution into  $\text{Na}^+$ , which is a spectator ion, and  $\text{ClO}^-$  ion, which is a weak base with  $K_b = 3.3 \times 10^{-7}$  (Equation 16.37).

**Plan:** From the pH, we can determine the equilibrium concentration of  $\text{OH}^-$ . We can then construct a table of initial and equilibrium concentrations in which the initial concentration of  $\text{ClO}^-$  is our unknown. We can calculate  $[\text{ClO}^-]$  using the equilibrium constant expression,  $K_b$ .

### Solve:

We can calculate  $[\text{OH}^-]$  by using either Equation 16.16 or Equation 16.20; we will use the latter method here:

This concentration is high enough that we can assume that Equation 16.37 is the only source of  $\text{OH}^-$ ; that is, we can neglect any  $\text{OH}^-$  produced by the autoionization of  $\text{H}_2\text{O}$ .

We now assume a value of  $x$  for the initial concentration of  $\text{ClO}^-$  and solve the equilibrium problem in the usual way.

$$\begin{aligned}\text{pOH} &= 14.00 - \text{pH} = 14.00 - 10.50 = 3.50 \\ [\text{OH}^-] &= 10^{-3.50} = 3.2 \times 10^{-4} \text{ M}\end{aligned}$$

	$\text{ClO}^-(aq)$	$+ \text{H}_2\text{O}(l) \rightleftharpoons$	$\text{HClO}(aq)$	$+ \text{OH}^-(aq)$
Initial	$x \text{ M}$	—	0	0
Change	$-3.2 \times 10^{-4} \text{ M}$	—	$+3.2 \times 10^{-4} \text{ M}$	$+3.2 \times 10^{-4} \text{ M}$
Equilibrium	$(x - 3.2 \times 10^{-4}) \text{ M}$	—	$3.2 \times 10^{-4} \text{ M}$	$3.2 \times 10^{-4} \text{ M}$

---

## Sample Exercise 16.16 Using pH to Determine the Concentration of a Salt

### Solution (Continued)

We now use the expression for the base-dissociation constant to solve for  $x$ :

$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{(3.2 \times 10^{-4})^2}{x - 3.2 \times 10^{-4}} = 3.3 \times 10^{-7}$$

Thus

$$x = \frac{(3.2 \times 10^{-4})^2}{3.3 \times 10^{-7}} + (3.2 \times 10^{-4}) = 0.31 \text{ M}$$

We say that the solution is 0.31  $M$  in NaClO even though some of the  $\text{ClO}^-$  ions have reacted with water. Because the solution is 0.31  $M$  in NaClO and the total volume of solution is 2.00 L, 0.62 mol of NaClO is the amount of the salt that was added to the water.

### Practice Exercise

A solution of  $\text{NH}_3$  in water has a pH of 11.17. What is the molarity of the solution?

**Answer:** 0.12  $M$

---

## Sample Exercise 16.17 Calculating $K_a$ or $K_b$ for a Conjugate Acid-Base Pair

Calculate (a) the base-dissociation constant,  $K_b$ , for the fluoride ion ( $F^-$ ); (b) the acid-dissociation constant,  $K_a$ , for the ammonium ion ( $NH_4^+$ ).

### Solution

**Analyze:** We are asked to determine dissociation constants for  $F^-$ , the conjugate base of HF, and  $NH_4^+$ , the conjugate acid of  $NH_3$ .

**Plan:** Although neither  $F^-$  nor  $NH_4^+$  appears in the tables, we can find the tabulated values for ionization constants for HF and  $NH_3$ , and use the relationship between  $K_a$  and  $K_b$  to calculate the ionization constants for each of the conjugates.

### Solve:

(a)  $K_a$  for the weak acid, HF, is given in Table 16.2 and Appendix D as  $K_a = 6.8 \times 10^{-4}$ . We can use Equation 16.40 to calculate  $K_b$  for the conjugate base,  $F^-$ :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

(b)  $K_b$  for  $NH_3$  is listed in Table 16.4 and in Appendix D as  $K_b = 1.8 \times 10^{-5}$ . Using Equation 16.40, we can calculate  $K_a$  for the conjugate acid,  $NH_4^+$ :

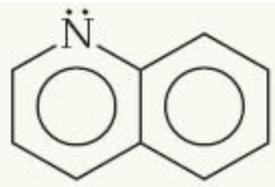
$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

---

## Sample Exercise 16.17 Calculating $K_a$ or $K_b$ for a Conjugate Acid-Base Pair

### Practice Exercise

- (a) Which of the following anions has the largest base-dissociation constant:  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ , or  $\text{N}_3^-$ ? (b) The base quinoline has the following structure:



Its conjugate acid is listed in handbooks as having a  $\text{p}K_a$  of 4.90. What is the base dissociation constant for quinoline?

**Answers:** (a)  $\text{PO}_4^{3-}$  ( $K_b = 2.4 \times 10^{-2}$ ), (b)  $7.9 \times 10^{-10}$

---

## Sample Exercise 16.18 Determining Whether Salt Solutions Are Acidic, Basic, or Neutral

Determine whether aqueous solutions of each of the following salts will be acidic, basic, or neutral: (a)  $\text{Ba}(\text{CH}_3\text{COO})_2$ , (b)  $\text{NH}_4\text{Cl}$ , (c)  $\text{CH}_3\text{NH}_3\text{Br}$ , (d)  $\text{KNO}_3$ , (e)  $\text{Al}(\text{ClO}_4)_3$ .

### Solution

**Analyze:** We are given the chemical formulas of five ionic compounds (salts) and asked whether their aqueous solutions will be acidic, basic, or neutral.

**Plan:** We can determine whether a solution of a salt is acidic, basic, or neutral by identifying the ions in solution and by assessing how each ion will affect the pH.

### Solve:

(a) This solution contains barium ions and acetate ions. The cation,  $\text{Ba}^{2+}$ , is an ion of one of the heavy alkaline earth metals and will therefore not affect the pH (summary point 4). The anion,  $\text{CH}_3\text{COO}^-$ , is the conjugate base of the weak acid  $\text{CH}_3\text{COOH}$  and will hydrolyze to produce  $\text{OH}^-$  ions, thereby making the solution basic (summary point 2).

(b) This solution contains  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions.  $\text{NH}_4^+$  is the conjugate acid of a weak base ( $\text{NH}_3$ ) and is therefore acidic (summary point 3).  $\text{Cl}^-$  is the conjugate base of a strong acid ( $\text{HCl}$ ) and therefore has no influence on the pH of the solution (summary point 1). Because the solution contains an ion that is acidic ( $\text{NH}_4^+$ ) and one that has no influence on pH ( $\text{Cl}^-$ ), the solution of  $\text{NH}_4\text{Cl}$  will be acidic.

(c) This solution contains  $\text{CH}_3\text{NH}_3^+$  and  $\text{Br}^-$  ions.  $\text{CH}_3\text{NH}_3^+$  is the conjugate acid of a weak base ( $\text{CH}_3\text{NH}_2$ , an amine) and is therefore acidic (summary point 3).  $\text{Br}^-$  is the conjugate base of a strong acid ( $\text{HBr}$ ) and is therefore pH-neutral (summary point 1). Because the solution contains one ion that is acidic and one that is neutral, the solution of  $\text{CH}_3\text{NH}_3\text{Br}$  will be acidic.

(d) This solution contains the  $\text{K}^+$  ion, which is a cation of group 1A, and the ion  $\text{NO}_3^-$ , which is the conjugate base of the strong acid  $\text{HNO}_3$ . Neither of the ions will react with water to any appreciable extent (summary points 1 and 4), making the solution neutral.

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## Sample Exercise 16.18 Determining Whether Salt Solutions Are Acidic, Basic, or Neutral

### Solution (Continued)

(e) This solution contains  $\text{Al}^{3+}$  and  $\text{ClO}_4^-$  ions. Cations, such as  $\text{Al}^{3+}$ , that are not in groups 1A or 2A are acidic (summary point 5). The  $\text{ClO}_4^-$  ion is the conjugate base of a strong acid ( $\text{HClO}_4$ ) and therefore does not affect pH (summary point 1). Thus, the solution of  $\text{Al}(\text{ClO}_4)_3$  will be acidic.

### Practice Exercise

In each of the following, indicate which salt in each of the following pairs will form the more acidic (or less basic) 0.010 M solution: (a)  $\text{NaNO}_3$ , or  $\text{Fe}(\text{NO}_3)_3$ ; (b)  $\text{KBr}$ , or  $\text{KBrO}$ ; (c)  $\text{CH}_3\text{NH}_3\text{Cl}$ , or  $\text{BaCl}_2$ , (d)  $\text{NH}_4\text{NO}_2$ , or  $\text{NH}_4\text{NO}_3$ .

**Answers:** (a)  $\text{Fe}(\text{NO}_3)_3$ , (b)  $\text{KBr}$ , (c)  $\text{CH}_3\text{NH}_3\text{Cl}$ , (d)  $\text{NH}_4\text{NO}_3$

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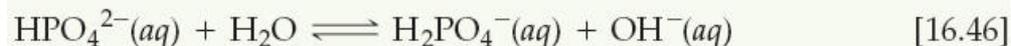
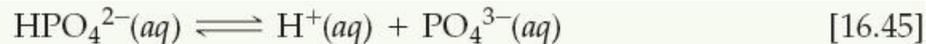
## Sample Exercise 16.19 Predicting Whether the Solution of an Amphiprotic Anion is Acidic or Basic

Predict whether the salt  $\text{Na}_2\text{HPO}_4$  will form an acidic solution or a basic solution on dissolving in water.

### Solution

**Analyze:** We are asked to predict whether a solution of  $\text{Na}_2\text{HPO}_4$  will be acidic or basic. This substance is an ionic compound composed of  $\text{Na}^+$  and  $\text{HPO}_4^{2-}$  ions.

**Plan:** We need to evaluate each ion, predicting whether each is acidic or basic. Because  $\text{Na}^+$  is a cation of group 1A, we know that it has no influence on pH. It is merely a spectator ion in acid–base chemistry. Thus, our analysis of whether the solution is acidic or basic must focus on the behavior of the  $\text{HPO}_4^{2-}$  ion. We need to consider the fact that  $\text{HPO}_4^{2-}$  can act as either an acid or a base.



The reaction with the larger equilibrium constant will determine whether the solution is acidic or basic

**Solve:** The value of  $K_a$  for Equation 16.45, as shown in Table 16.3, is  $4.2 \times 10^{-13}$ . We must calculate the value of  $K_b$  for Equation 16.46 from the value of  $K_a$  for its conjugate acid,  $\text{H}_2\text{PO}_4^-$ . We make use of the relationship shown in Equation 16.40.

$$K_a \times K_b = K_w$$

We want to know  $K_b$  for the base  $\text{HPO}_4^{2-}$ , knowing the value of  $K_a$  for the conjugate acid  $\text{H}_2\text{PO}_4^-$ :

$$K_b(\text{HPO}_4^{2-}) \times K_a(\text{H}_2\text{PO}_4^-) = K_w = 1.0 \times 10^{-14}$$

Because  $K_a$  for  $\text{H}_2\text{PO}_4^-$  is  $6.2 \times 10^{-8}$  (Table 16.3), we calculate  $K_b$  for  $\text{H}_2\text{PO}_4^{2-}$  to be  $1.6 \times 10^{-7}$ . This is more than  $10^5$  times larger than  $K_a$  for  $\text{H}_2\text{PO}_4^{2-}$ ; thus, the reaction shown in Equation 16.46 predominates over that in Equation 16.45, and the solution will be basic.

---

## Sample Exercise 16.19 Predicting Whether the Solution of an Amphiprotic Anion is Acidic or Basic

### Practice Exercise

Predict whether the dipotassium salt of citric acid ( $\text{K}_2\text{HC}_6\text{H}_5\text{O}_7$ ) will form an acidic or basic solution in water (see Table 16.3 for data).

**Answer:** acidic

---

## Sample Exercise 16.20 Predicting Relative Acidities from Composition and Structure

Arrange the compounds in each of the following series in order of increasing acid strength:

(a)  $\text{AsH}_3$ ,  $\text{HI}$ ,  $\text{NaH}$ ,  $\text{H}_2\text{O}$ ; (b)  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SeO}_3$ ,  $\text{H}_2\text{SeO}_4$ .

### Solution

**Analyze:** We are asked to arrange two sets of compounds in order from weakest acid to strongest acid. In (a), the substances are binary compounds containing H, whereas in (b) the substances are oxyacids.

**Plan:** For the binary compounds in part (a), we will consider the electronegativities of As, I, Na, and O relative to H. A higher electronegativity will cause the H to have a higher partial positive charge, causing the compound to be more acidic. For the oxyacids in part (b), we will consider both the relative electronegativities of the central atom (S and Se) and the number of oxygen atoms bonded to the central atom.

### Solve:

(a) Because Na is on the left side of the periodic table, we know that it has a very low electronegativity. As a result, the hydrogen in NaH carries a negative charge. Thus NaH should be the least acidic (most basic) compound on the list. Because arsenic is less electronegative than oxygen, we might expect that  $\text{AsH}_3$  would be a weak base toward water. We would make the same prediction by an extension of the trends shown in Figure 16.12. Further, we expect that the binary hydrogen compounds of the halogens, as the most electronegative element in each period, will be acidic relative to water. In fact, HI is one of the strong acids in water. Thus the order of increasing acidity is  $\text{NaH} < \text{AsH}_3 < \text{H}_2\text{O} < \text{HI}$ .

(b) The acids  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SeO}_4$  have the same number of O atoms and OH groups. In such cases, the acid strength increases with increasing electronegativity of the central atom. Because S is more electronegative than Se, we predict that  $\text{H}_2\text{SO}_4$  is more acidic than  $\text{H}_2\text{SeO}_4$ . Next, we can compare  $\text{H}_2\text{SeO}_4$  and  $\text{H}_2\text{SeO}_3$ . For acids with the same central atom, the acidity increases as the number of oxygen atoms bonded to the central atom increases. Thus,  $\text{H}_2\text{SeO}_4$  should be a stronger acid than  $\text{H}_2\text{SeO}_3$ . Thus, we predict the order of increasing acidity to be  $\text{H}_2\text{SeO}_3 < \text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4$ .

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## Sample Exercise 16.20 Predicting Relative Acidities from Composition and Structure

### Practice Exercise

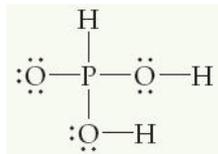
In each of the following pairs choose the compound that leads to the more acidic (or less basic) solution: **(a)** HBr, HF; **(b)** PH<sub>3</sub>, H<sub>2</sub>S; **(c)** HNO<sub>2</sub>, HNO<sub>3</sub>; **(d)** H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SeO<sub>3</sub>.

**Answers:** **(a)** HBr, **(b)** H<sub>2</sub>S, **(c)** HNO<sub>3</sub>, **(d)** H<sub>2</sub>SO<sub>3</sub>

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## Sample Integrated Exercise Putting Concepts Together

Phosphorous acid ( $\text{H}_3\text{PO}_3$ ) has the following Lewis structure



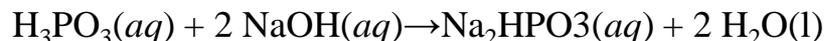
**(a)** Explain why  $\text{H}_3\text{PO}_3$  is diprotic and not triprotic. **(b)** A 25.0-mL sample of a solution of  $\text{H}_3\text{PO}_3$  is titrated with 0.102 M NaOH. It requires 23.3 mL of NaOH to neutralize both acidic protons. What is the molarity of the  $\text{H}_3\text{PO}_3$  solution? **(c)** The original solution from part (b) has a pH of 1.59. Calculate the percent ionization and  $K_{a1}$  for  $\text{H}_3\text{PO}_3$ , assuming that  $K_{a1} \gg K_{a2}$ . **(d)** How does the osmotic pressure of a 0.050 M solution of HCl compare qualitatively with that of a 0.050 M solution of  $\text{H}_3\text{PO}_3$ ? Explain.

### Solution

We will use what we have learned about molecular structure and its impact on acidic behavior to answer part (a). We will then use stoichiometry and the relationship between pH and  $[\text{H}^+]$  to answer parts (b) and (c). Finally, we will consider acid strength in order to compare the colligative properties of the two solutions in part (d).

**(a)** Acids have polar H—X bonds. From Figure 8.6 we see that the electronegativity of H is 2.1 and that of P is also 2.1. Because the two elements have the same electronegativity, the H—P bond is nonpolar. (Section 8.4) Thus, this H cannot be acidic. The other two H atoms, however, are bonded to O, which has an electronegativity of 3.5. The H—O bonds are therefore polar, with H having a partial positive charge. These two H atoms are consequently acidic.

**(b)** The chemical equation for the neutralization reaction is



## Sample Integrated Exercise Putting Concepts Together

### Solution (Continued)

From the definition of molarity,  $M = \text{mol/L}$ , we see that  $\text{moles} = M \times L$ . (Section 4.5) Thus, the number of moles of NaOH added to the solution is  $(0.0233 \text{ L})(0.102 \text{ mol/L}) = 2.38 \times 10^{-3} \text{ mol NaOH}$ . The balanced equation indicates that 2 mol of NaOH is consumed for each mole of  $\text{H}_3\text{PO}_3$ . Thus, the number of moles of  $\text{H}_3\text{PO}_3$  in the sample is

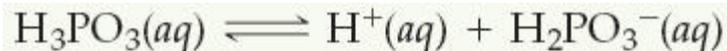
$$(2.38 \times 10^{-3} \text{ mol NaOH}) \left( \frac{1 \text{ mol H}_3\text{PO}_3}{2 \text{ mol NaOH}} \right) = 1.19 \times 10^{-3} \text{ mol H}_3\text{PO}_3$$

The concentration of the  $\text{H}_3\text{PO}_3$  solution, therefore, equals  $(1.19 \times 10^{-3} \text{ mol}) / (0.0250 \text{ L}) = 0.0476 \text{ M}$ .

(c) From the pH of the solution, 1.59, we can calculate at equilibrium.

$$[\text{H}^+] = \text{antilog}(-1.59) = 10^{-1.59} = 0.026 \text{ M (two significant figures)}$$

Because  $K_{a1} \gg K_{a2}$ , the vast majority of the ions in solution are from the first ionization step of the acid.



Because one  $\text{H}_2\text{PO}_3^-$  ion forms for each  $\text{H}^+$  ion formed, the equilibrium concentrations of  $\text{H}^+$  and  $\text{H}_2\text{PO}_3^-$  are equal:  $[\text{H}^+] = [\text{H}_2\text{PO}_3^-] = 0.026 \text{ M}$ . The equilibrium concentration of  $\text{H}_3\text{PO}_3$  equals the initial concentration minus the amount that ionizes to form  $\text{H}^+$  and  $\text{H}_2\text{PO}_3^-$ :  $[\text{H}_3\text{PO}_3] = 0.0476 \text{ M} - 0.026 \text{ M} = 0.022 \text{ M}$  (two significant figures). These results can be tabulated as follows:

	$\text{H}_3\text{PO}_3(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	+	$\text{H}_2\text{PO}_3^-(\text{aq})$
Initial	0.0476 M		0		0
Change	-0.026 M		+0.026 M		+0.026 M
Equilibrium	0.022 M		0.026 M		0.026 M

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## Sample Integrated Exercise Putting Concepts Together

### Solution (Continued)

The percent ionization is

$$\text{Percent ionization} = \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{H}_3\text{PO}_3]_{\text{initial}}} \times 100\% = \frac{0.026 \text{ M}}{0.0476 \text{ M}} \times 100\% = 55\%$$

The first acid-dissociation constant is

$$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_3^-]}{[\text{H}_3\text{PO}_3]} = \frac{(0.026)(0.026)}{0.022} = 0.031$$

(d) Osmotic pressure is a colligative property and depends on the total concentration of particles in solution. (Section 13.5) Because HCl is a strong acid, a 0.050 M solution will contain 0.050 M  $\text{H}^+(aq)$  and 0.050 M  $\text{Cl}^-(aq)$ , or a total of 0.100 mol/L of particles. Because  $\text{H}_3\text{PO}_3$  is a weak acid, it ionizes to a lesser extent than HCl, and, hence, there are fewer particles in the  $\text{H}_3\text{PO}_3$  solution. As a result, the  $\text{H}_3\text{PO}_3$  solution will have the lower osmotic pressure.

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