

Sample Exercise 16.1 Identifying Conjugate Acids and Bases

- (a) What is the conjugate base of HClO_4 , H_2S , PH_4^+ , HCO_3^- ?
(b) What is the conjugate acid of CN^- , SO_4^{2-} , H_2O , HCO_3^- ?

Solution

Analyze We are asked to give the conjugate base for several acids and the conjugate acid for several bases.

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) If we remove a proton from HClO_4 , we obtain ClO_4^- , which is its conjugate base. The other conjugate bases are HS^- , PH_3 , and CO_3^{2-} .
(b) If we add a proton to CN^- , we get HCN , its conjugate acid. The other conjugate acids are HSO_4^- , H_3O^+ , and H_2CO_3 . Notice that the hydrogen carbonate ion (HCO_3^-) is amphiprotic. It can act as either an acid or a base.

Practice Exercise 1

Consider the following equilibrium reaction:



Sample Exercise 16.1 Identifying Conjugate Acids and Bases

Continued

Which substances are acting as acids in the reaction?

- (a) HSO_4^- and OH^-
- (b) HSO_4^- and H_2O
- (c) OH^- and SO_4^{2-}
- (d) SO_4^{2-} and H_2O
- (e) None of the substances are acting as acids in this reaction.

Practice Exercise 2

Write the formula for the conjugate acid of each of the following: HSO_3^- , F^- , PO_4^{3-} , CO .

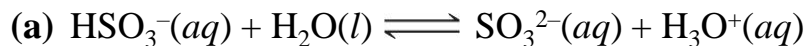
Sample Exercise 16.2 Writing Equations for Proton-Transfer Reactions

The hydrogen sulfite ion (HSO_3^-) is amphiprotic. Write an equation for the reaction of HSO_3^- with water (a) in which the ion acts as an acid and (b) 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 HSO_3^- and water, one in which HSO_3^- should donate a proton to water, thereby acting as a Brønsted–Lowry acid, and one in which 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.

Solve



The conjugate pairs in this equation are HSO_3^- (acid) and SO_3^{2-} (conjugate base), and H_2O (base) and H_3O^+ (conjugate acid).

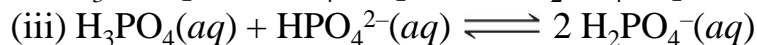
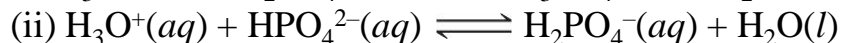
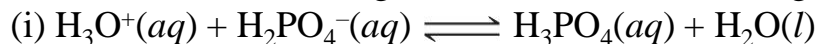


The conjugate pairs in this equation are H_2O (acid) and OH^- (conjugate base), and HSO_3^- (base) and H_2SO_3 (conjugate acid).

Practice Exercise 1

The dihydrogen phosphate ion, H_2PO_4^- , is amphiprotic.

In which of the following reactions is this ion serving as a base?



(a) i only (b) i and ii (c) i and iii (d) ii and iii (e) i, ii, and iii

Sample Exercise 16.2 Writing Equations for Proton-Transfer Reactions

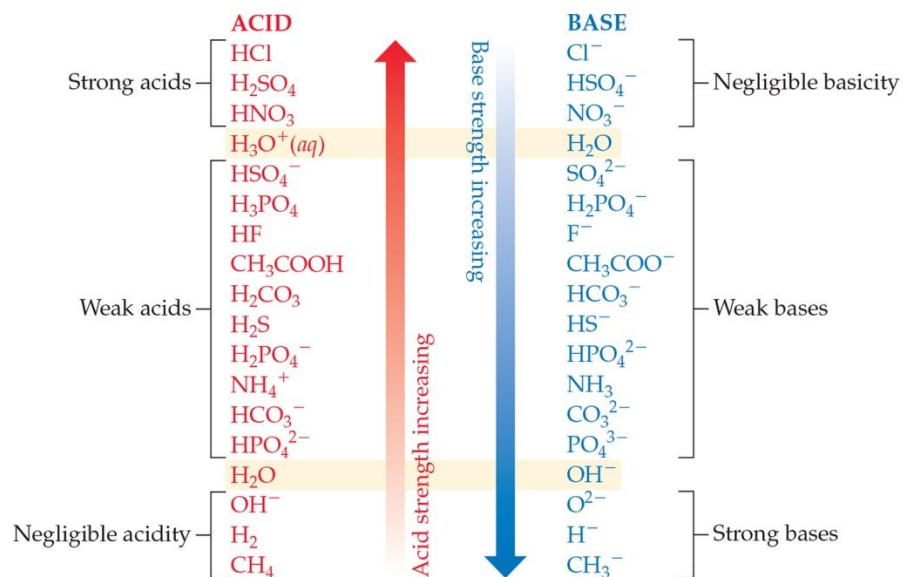
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Practice Exercise 2

When lithium oxide (Li_2O) is dissolved in water, the solution turns basic from the reaction of the oxide ion (O^{2-}) with water. Write the equation for this reaction and identify the conjugate acid–base pairs.

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 to the left ($K_c < 1$) or to the right ($K_c > 1$):



Solution

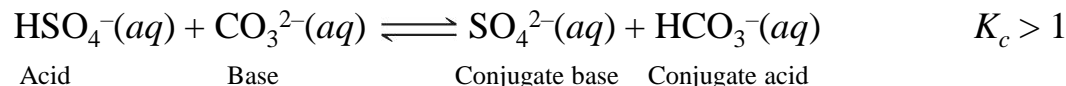
Analyze We are asked to predict whether an equilibrium lies to the right, favoring products, or to the left, favoring reactants.

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 CO_3^{2-} , the base in the forward reaction, and SO_4^{2-} , the conjugate base of HSO_4^- . We can find the relative positions of these two bases in Figure 16.4 to determine which is the stronger base.

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

Continued

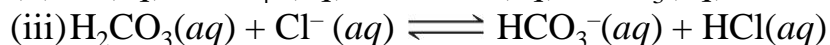
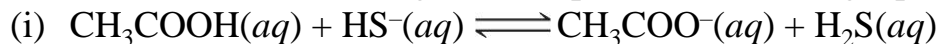
Solve The CO_3^{2-} ion appears lower in the right-hand column in Figure 16.4 and is therefore a stronger base than SO_4^{2-} . Therefore, CO_3^{2-} will get the proton preferentially to become HCO_3^- , while SO_4^{2-} will remain mostly unprotonated. The resulting equilibrium lies to the right, favoring products (that is, $K_c > 1$):



Comment Of the two acids HSO_4^- and HCO_3^- , the stronger one (HSO_4^-) gives up a proton more readily, and the weaker one (HCO_3^-) 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 1

Based on information in Figure 16.4, place the following equilibria in order from smallest to largest value of K_c :



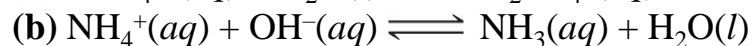
(a) $i < ii < iii$ (b) $ii < i < iii$ (c) $iii < i < ii$ (d) $ii < iii < i$ (e) $iii < ii < i$

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

Continued

Practice Exercise 2

For each reaction, use Figure 16.4 to predict whether the equilibrium lies to the left or to the right:



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

Calculate the values of $[H^+]$ and $[OH^-]$ in a neutral aqueous 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 1

In a certain acidic solution at 25 °C, $[H^+]$ is 100 times greater than $[OH^-]$. What is the value for $[OH^-]$ for the solution?

- (a) $1.0 \times 10^{-8} M$ (b) $1.0 \times 10^{-7} M$ (c) $1.0 \times 10^{-6} M$
(d) $1.0 \times 10^{-2} M$ (e) $1.0 \times 10^{-9} M$

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

Continued

Practice Exercise 2

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic at 25 °C:

- (a) $[H^+] = 4 \times 10^{-9} M$;
- (b) $[OH^-] = 1 \times 10^{-7} M$;
- (c) $[OH^-] = 1 \times 10^{-13} M$.

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 $[H^+]$ 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

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

This solution is basic because

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

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

Continued

(b) In this instance

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

This solution is acidic because

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

Practice Exercise 1

A solution has $[OH^-] = 4.0 \times 10^{-8}$. What is the value of $[H^+]$ for the solution?

- (a) $2.5 \times 10^{-8} M$ (b) $4.0 \times 10^{-8} M$ (c) $2.5 \times 10^{-7} M$
(d) $2.5 \times 10^{-6} M$ (e) $4.0 \times 10^{-6} M$

Practice Exercise 2

Calculate the concentration of $OH^-(aq)$ in a solution in which

- (a) $[H^+] = 2 \times 10^{-6} M$; (b) $[H^+] = [OH^-]$;
(c) $[H^+] = 200 \times [OH^-]$.

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

Calculate the pH values for the two solutions of 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 $1.0 \times 10^{-12} M$, so that

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

Because 1.0×10^{-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 1×10^{-6} and 1×10^{-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 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.

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

Continued

Practice Exercise 1

A solution at 25 °C has $[OH^-] = 6.7 \times 10^{-3}$. What is the pH of the solution?

(a) 0.83 (b) 2.2 (c) 2.17 (d) 11.83 (e) 12

Practice Exercise 2

(a) In a sample of lemon juice, $[H^+] = 3.8 \times 10^{-4} M$. What is the pH?

(b) A commonly available window-cleaning solution has $[OH^-] = 1.9 \times 10^{-6} M$. What is the pH at 25 °C?

Sample Exercise 16.7 Calculating $[H^+]$ from pOH

A sample of freshly pressed apple juice has a pOH of 10.24. Calculate $[H^+]$.

Solution

Analyze We need to calculate $[H^+]$ from pOH.

Plan We will first use Equation 16.20, $pH + pOH = 14.00$, to calculate pH from pOH. Then we will use Equation 16.17 to determine the concentration of H^+ .

Solve From Equation 16.20, we have

$$\begin{aligned}pH &= 14.00 - pOH \\pH &= 14.00 - 10.24 = 3.76\end{aligned}$$

Next we use Equation 16.17:

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

Thus,

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

To find $[H^+]$, we need to determine the *antilogarithm* of -3.76 . Your calculator will show this command as 10^x or INV log (these functions are usually above the log key). We use this function to perform the calculation:

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

Sample Exercise 16.7 Calculating $[H^+]$ from pOH

Continued

Comment 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 $1.0 \times 10^{-3} M$ and $1.0 \times 10^{-4} M$. Our calculated $[H^+]$ falls within this estimated range.

Practice Exercise 1

A solution at 25 °C has pOH = 10.53. Which of the following statements is or are true?

- (i) The solution is acidic.
 - (ii) The pH of the solution is $14.00 - 10.53$.
 - (iii) For this solution, $[OH^-] = 10^{-10.53} M$.
- (a) Only one of the statements is true.
(b) Statements (i) and (ii) are true.
(c) Statements (i) and (iii) are true.
(d) Statements (ii) and (iii) are true.
(e) All three statements are true.

Practice Exercise 2

A solution formed by dissolving an antacid tablet has a pOH of 4.82. Calculate $[H^+]$.

Sample Exercise 16.8 Calculating the pH of a Strong Acid Solution

What is the pH of a 0.040 *M* solution of HClO₄?

Solution

Analyze and Plan Because HClO₄ is a strong acid, it is completely ionized, giving $[\text{H}^+] = [\text{ClO}_4^-] = 0.040 \text{ M}$.

Solve

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

Check Because $[\text{H}^+]$ lies between 1×10^{-2} and 1×10^{-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 1

Order the following three solutions from smallest to largest pH:

(i) 0.20 *M* HClO₃ (ii) 0.0030 *M* HNO₃ (iii) 1.50 *M* HCl

(a) i < ii < iii (b) ii < i < iii (c) iii < i < ii

(d) ii < iii < i (e) iii < ii < i

Practice Exercise 2

An aqueous solution of HNO₃ has a pH of 2.34. What is the concentration of the acid?

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)₂?

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⁺] and then use Equation 16.17 to calculate the pH. Alternatively, we could use [OH⁻] to calculate pOH and then use Equation 16.20 to calculate the pH.

Solve

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

Method 1:

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.028} = 3.57 \times 10^{-13} \text{ M}$$

$$\text{pH} = -\log(3.57 \times 10^{-13}) = 12.45$$

Method 2:

$$\text{pOH} = -\log(0.028) = 1.55$$

$$\text{pH} = 14.00 - \text{pOH} = 12.45$$

Sample Exercise 16.9 Calculating the pH of a Strong Base

Continued

(b) $\text{Ca}(\text{OH})_2$ is a strong base that dissociates in water to give *two* OH^- ions per formula unit. Thus, the concentration of $\text{OH}^-(aq)$ for the solution in part (b) is $2 \times (0.0011 M) = 0.0022 M$.

Method 1:

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.0022} = 4.55 \times 10^{-12} M$$

$$\text{pH} = -\log(4.55 \times 10^{-12}) = 11.34$$

Method 2:

$$\text{pOH} = -\log(0.0022) = 2.66$$

$$\text{pH} = 14.00 - \text{pOH} = 11.34$$

Practice Exercise 1

Order the following three solutions from smallest to largest pH:

(i) $0.030 M \text{Ba}(\text{OH})_2$ (ii) $0.040 M \text{KOH}$ (iii) pure water.

(a) $i < ii < iii$ (b) $ii < i < iii$ (c) $iii < i < ii$ (d) $ii < iii < i$ (e) $iii < ii < i$

Practice Exercise 2

What is the concentration of a solution of (a) KOH for which the pH is 11.89, (b) $\text{Ca}(\text{OH})_2$ for which the pH is 11.68?

Sample Exercise 16.10 Calculating K_a from Measured pH

A student prepared a 0.10 M solution of formic acid (HCOOH) and found its pH at 25 °C 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 similar to the equilibrium problems in Chapter 15. We can solve this problem using the method outlined in Sample Exercise 15.8, 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:



The equilibrium-constant expression is:

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

Sample Exercise 16.10 Calculating K_a from Measured pH

Continued

From the measured pH, we can calculate $[H^+]$:

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

$$\log [H^+] = -2.38$$

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

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



Initial concentration (M)	0.10	0	0
Change in concentration (M)	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
Equilibrium concentration (M)	$(0.10 - 4.2 \times 10^{-3})$	4.2×10^{-3}	4.2×10^{-3}

Notice that we have neglected the very small concentration of $H^+(aq)$ due to H_2O autoionization. Notice also that the amount of $HCOOH$ 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 $0.10 M$:

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

Sample Exercise 16.10 Calculating K_a from Measured pH

Continued

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

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

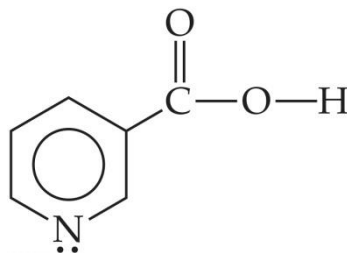
Check The magnitude of our answer is reasonable because K_a for a weak acid is usually between 10^{-2} and 10^{-10} .

Practice Exercise 1

A 0.50 M solution of an acid HA has pH = 2.24. What is the value of K_a for the acid? (a) 1.7×10^{-12} (b) 3.3×10^{-5} (c) 6.6×10^{-5} (d) 5.8×10^{-3} (e) 1.2×10^{-2}

Practice Exercise 2

Niacin, one of the B vitamins, has the molecular structure shown at the right. A 0.020 M solution of niacin has a pH of 3.26. What is the acid-dissociation constant for niacin?



Sample Exercise 16.11 Calculating Percent Ionization

As calculated in Sample Exercise 16.10, a 0.10 *M* solution of formic acid (HCOOH) contains $4.2 \times 10^{-3} \text{ M H}^+(\text{aq})$. 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 $\text{H}^+(\text{aq})$ and asked to determine the percent ionization of the acid.

Plan The percent ionization is given by Equation 16.27.

Solve

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

Practice Exercise 1

A 0.077 *M* solution of an acid HA has pH = 2.16. What is the percentage of the acid that is ionized?

(a) 0.090% (b) 0.69% (c) 0.90% (d) 3.6% (e) 9.0%

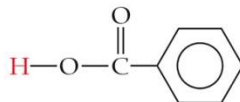
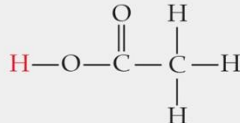
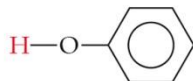
Practice Exercise 2

A 0.020 *M* solution of niacin (see Sample Exercise 16.10) has a pH of 3.26. Calculate the percent ionization of the niacin.

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 .)

TABLE 16.2 Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous (HClO ₂)	H—O—Cl—O	ClO ₂ ⁻	1.0×10^{-2}
Hydrofluoric (HF)	H—F	F ⁻	6.8×10^{-4}
Nitrous (HNO ₂)	H—O—N=O	NO ₂ ⁻	4.5×10^{-4}
Benzoic (C ₆ H ₅ COOH)		C ₆ H ₅ COO ⁻	6.3×10^{-5}
Acetic (CH ₃ COOH)		CH ₃ COO ⁻	1.8×10^{-5}
Hypochlorous (HOCl)	H—O—Cl	OCl ⁻	3.0×10^{-8}
Hydrocyanic (HCN)	H—C≡N	CN ⁻	4.9×10^{-10}
Phenol (HOC ₆ H ₅)		C ₆ H ₅ O ⁻	1.3×10^{-10}

*The proton that ionizes is shown in red.

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 4.9×10^{-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.

Sample Exercise 16.12 Using K_a to Calculate pH

Continued

Solve Writing both the chemical equation for the ionization reaction that forms $\text{H}^+(\text{aq})$ 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 concentrations of the species involved in the equilibrium reaction, letting $x = [\text{H}^+]$ at equilibrium:

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

Substituting the equilibrium concentrations 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

Continued

We next make the simplifying approximation that x , the amount of acid that dissociates, is small compared with the initial concentration of acid, $0.20 - x \approx 0.20$. Thus,

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

Solving for x , we have:

$$\begin{aligned}x^2 &= (0.20)(4.9 \times 10^{-10}) = 0.98 \times 10^{-10} \\x &= \sqrt{0.98 \times 10^{-10}} = 9.9 \times 10^{-6} M = [H^+]\end{aligned}$$

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

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

Sample Exercise 16.12 Using K_a to Calculate pH

Continued

Practice Exercise 1

What is the pH of a 0.40 M solution of benzoic acid, C_6H_5COOH ? (The K_a value for benzoic acid is given in Table 16.2.)

(a) 2.30 (b) 2.10 (c) 1.90 (d) 4.20 (e) 4.60

Practice Exercise 2

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

Sample Exercise 16.13 Using the Quadratic Equation to Calculate pH and Percent Ionization

Calculate the pH and percentage of HF molecules ionized in a 0.10 *M* HF solution.

Solution

Analyze We are asked to calculate the percent ionization of a solution of HF. From Appendix D, we find $K_a = 6.8 \times 10^{-4}$.

Plan We approach this problem as for previous equilibrium problems: We write the chemical equation for the equilibrium and tabulate 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 of H^+ .

Solve

The equilibrium reaction and equilibrium concentrations are as follows:



Initial concentration (<i>M</i>)	0.10	0	0
Change in concentration (<i>M</i>)	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium concentration (<i>M</i>)	(0.10 - <i>x</i>)	<i>x</i>	<i>x</i>

Sample Exercise 16.13 Using the Quadratic Equation to Calculate pH and Percent Ionization

Continued

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 $0.10 - x \approx 0.10$ (that is, by neglecting the concentration of acid that ionizes), we obtain:

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

Because this approximation is greater than 5% of $0.10 M$, however, we should work the problem in standard quadratic form. Rearranging, we have:

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

Substituting these values in the standard quadratic formula gives:

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

Sample Exercise 16.13 Using the Quadratic Equation to Calculate pH and Percent Ionization

Continued

Of the two solutions, only the positive value for x is chemically reasonable. From that value, we can determine $[\text{H}^+]$ and hence the pH:

$$x = [\text{H}^+] = [\text{F}^-] = 7.9 \times 10^{-3} \text{ M}, \text{ so } \text{pH} = -\log[\text{H}^+] = 2.10$$

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

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

Practice Exercise 1

What is the pH of a 0.010 M solution of HF?

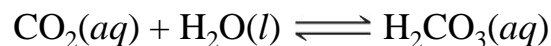
(a) 1.58 (b) 2.10 (c) 2.30 (d) 2.58 (e) 2.64

Practice Exercise 2

In Practice Exercise 2 for Sample 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) $1.0 \times 10^{-3} \text{ M}$.

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

The solubility of CO_2 in water at 25°C and 0.1 atm is 0.0037 M . The common practice is to assume that all the dissolved CO_2 is in the form of carbonic acid (H_2CO_3), which is produced in the reaction



What is the pH of a 0.0037 M solution of H_2CO_3 ?

Solution

Analyze We are asked to determine the pH of a 0.0037 M solution of a polyprotic acid.

Plan H_2CO_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.

TABLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

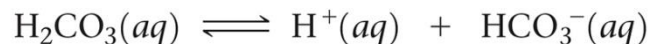
Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$\text{HOOC}-\text{COOH}$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$\text{C}_2\text{H}_2\text{O}_2(\text{COOH})_2$	1.0×10^{-3}	4.6×10^{-5}	

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

Continued

Solve

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



Initial concentration (<i>M</i>)	0.0037	0	0
Change in concentration (<i>M</i>)	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium concentration (<i>M</i>)	(0.0037 - <i>x</i>)	<i>x</i>	<i>x</i>

The equilibrium-constant expression is:

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

Solving this quadratic equation, we get:

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

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

Continued

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

$$0.0037 - x \simeq 0.0037$$

Thus,

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

Solving for x , we have:

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

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

Because we get the same value (to two significant figures) our simplifying assumption was justified. The pH is therefore:

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

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

Continued

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



Initial concentration (M)	4.0×10^{-5}	4.0×10^{-5}	0
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$(4.0 \times 10^{-5} - y)$	$(4.0 \times 10^{-5} + y)$	y

Assuming that y is small relative to 4.0×10^{-5} , we have:

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

$$y = 5.6 \times 10^{-11} \text{ M} = [\text{CO}_3^{2-}]$$

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

Continued

We see that the value for y is indeed very small compared with 4.0×10^{-5} , showing that our assumption was justified. It also shows that the ionization of HCO_3^- is negligible relative to that of H_2CO_3 , as far as production of H^+ is concerned. However, it is the *only* source of 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 CO_2 is in the form of CO_2 or H_2CO_3 , only a small fraction ionizes to form H^+ and HCO_3^- , and an even smaller fraction ionizes to give CO_3^{2-} . Notice also that $[\text{CO}_3^{2-}]$ is numerically equal to K_{a2} .

Practice Exercise 1

What is the pH of a 0.28 M solution of ascorbic acid (Vitamin C)? (See Table 16.3 for K_{a1} and K_{a2} .)

(a) 2.04 (b) 2.32 (c) 2.82 (d) 4.65 (e) 6.17

Practice Exercise 2

(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.

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

Calculate the concentration of OH^- in a 0.15 M solution of NH_3 .

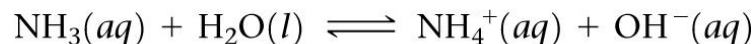
Solution

Analyze We are given the concentration of a weak base and asked to determine the concentration of OH^- .

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

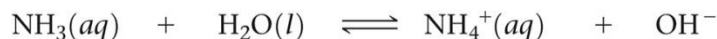
Solve

The ionization reaction and equilibrium constant expression are:



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

Ignoring the concentration of H_2O because it is not involved in the equilibrium-constant expression, we see that the equilibrium concentrations are:



Initial concentration (M)	0.15	—	0	0
Change in concentration (M)	$-x$	—	$+x$	$+x$
Equilibrium concentration (M)	$(0.15 - x)$	—	x	x

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

Continued

Inserting these quantities into the equilibrium-constant expression gives:

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

Because K_b is small, the amount of NH_3 that reacts with water is much smaller than the NH_3 concentration, and so we can neglect x relative to 0.15 M . Then we have:

$$\begin{aligned}\frac{x^2}{0.15} &= 1.8 \times 10^{-5} \\ x^2 &= (0.15)(1.8 \times 10^{-5}) = 2.7 \times 10^{-6} \\ x &= [\text{NH}_4^+] = [\text{OH}^-] = \sqrt{2.7 \times 10^{-6}} = 1.6 \times 10^{-3} \text{ M}\end{aligned}$$

Check The value obtained for x is only about 1% of the 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 NH_3 contains $[\text{OH}^-] = 1.6 \times 10^{-3} \text{ M}$. 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.

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

Continued

Practice Exercise 1

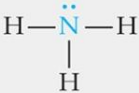

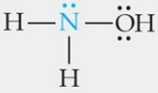
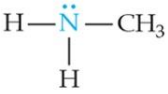

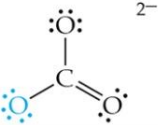

What is the pH of a 0.65 M solution of pyridine, $\text{C}_5\text{H}_5\text{N}$? (See Table 16.4 for K_b .)

(a) 4.48 (b) 8.96 (c) 9.52 (d) 9.62 (e) 9.71

Practice Exercise 2

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

TABLE 16.4 Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)		NH_4^+	1.8×10^{-5}
Pyridine ($\text{C}_5\text{H}_5\text{N}$)		$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}
Hydroxylamine (HONH_2)		HONH_3^+	1.1×10^{-8}
Methylamine (CH_3NH_2)		CH_3NH_3^+	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	3.3×10^{-7}

*The atom that accepts the proton is shown in blue.

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 added to the water.

Solution

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

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

Solve

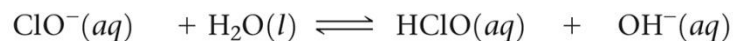
We can calculate $[\text{OH}^-]$ by using either Equation 16.16 or Equation 16.20; we will use the latter method here:

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

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

Continued

This concentration is high enough that we can assume that Equation 16.37 is the only source of OH^- ; that is, we can neglect any OH^- produced by the autoionization of H_2O . We now assume a value of x for the initial concentration of ClO^- and solve the equilibrium problem in the usual way.



Initial concentration (M)	x	—	0	0
Change in concentration (M)	-3.2×10^{-4}	—	$+3.2 \times 10^{-4}$	$+3.2 \times 10^{-4}$
Equilibrium concentration (M)	$(x - 3.2 \times 10^{-4})$	—	3.2×10^{-4}	3.2×10^{-4}

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

$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{(3.2 \times 10^{-4})^2}{x - 3.2 \times 10^{-4}} = 3.3 \times 10^{-7}$$
$$x = \frac{(3.2 \times 10^{-4})^2}{3.3 \times 10^{-7}} + (3.2 \times 10^{-4}) = 0.31 \text{ M}$$

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

Continued

We say that the solution is 0.31 *M* in NaClO even though some of the 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 1

The benzoate ion, C₆H₅COO⁻, is a weak base with $K_b = 1.6 \times 10^{-10}$. How many moles of sodium benzoate are present in 0.50 L of a solution of NaC₆H₅COO if the pH is 9.04?

(a) 0.38 (b) 0.66 (c) 0.76 (d) 1.5 (e) 2.9

Practice Exercise 2

What is the molarity of an aqueous NH₃ solution that has a pH of 11.17?

Sample Exercise 16.17 Calculating K_a or K_b for a Conjugate Acid–Base Pair

Calculate (a) K_b for the fluoride ion, (b) K_a for the ammonium ion.

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 .

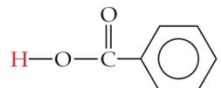
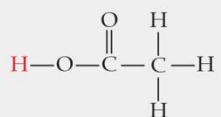
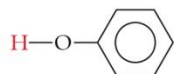
Plan We can use the tabulated K values for HF and NH_3 and the relationship between K_a and K_b to calculate the dissociation constants for their conjugates, F^- and NH_4^+ .

Solve

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

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

TABLE 16.2 Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous ($HClO_2$)	$H-O-Cl-O$	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	$H-F$	F^-	6.8×10^{-4}
Nitrous (HNO_2)	$H-O-N=O$	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)		CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	$H-O-Cl$	OCl^-	3.0×10^{-8}
Hydrocyanic (HCN)	$H-C \equiv N$	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	1.3×10^{-10}

*The proton that ionizes is shown in red.

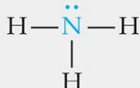

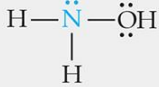
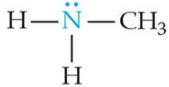

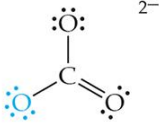

Sample Exercise 16.17 Calculating K_a or K_b for a Conjugate Acid–Base Pair

Continued

(b) For NH_3 , Table 16.4 and Appendix D give $K_b = 1.8 \times 10^{-5}$, and this value in Equation 16.40 gives us K_a for the conjugate acid, NH_4^+ :

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

TABLE 16.4 Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)		NH_4^+	1.8×10^{-5}
Pyridine ($\text{C}_5\text{H}_5\text{N}$)		$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}
Hydroxylamine (HONH_2)		HONH_3^+	1.1×10^{-8}
Methylamine (CH_3NH_2)		CH_3NH_3^+	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	3.3×10^{-7}

*The atom that accepts the proton is shown in blue.

Sample Exercise 16.17 Calculating K_a or K_b for a Conjugate Acid–Base Pair

Continued

Check The respective K values for F^- and NH_4^+ are listed in Table 16.5, where we see that the values calculated here agree with those in Table 16.5.

TABLE 16.5 Some Conjugate Acid–Base Pairs

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

Practice Exercise 1

By using information from Appendix D, put the following three substances in order of weakest to strongest base:

(i) $(CH_3)_3N$, (ii) $HCOO^-$, (iii) BrO^- .

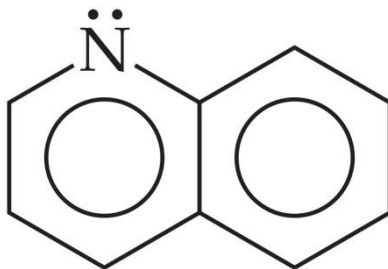
(a) $i < ii < iii$ (b) $ii < i < iii$ (c) $iii < i < ii$ (d) $ii < iii < i$ (e) $iii < ii < i$

Sample Exercise 16.17 Calculating K_a or K_b for a Conjugate Acid–Base Pair

Continued

Practice Exercise 2

- (a) Based on information in Appendix D, which of these anions has the largest base-dissociation constant: NO_2^- , PO_4^{3-} , or N_3^- ?
- (b) The base quinoline has the 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?

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

Determine whether aqueous solutions of each of these salts are acidic, basic, or neutral: (a) $\text{Ba}(\text{CH}_3\text{COO})_2$, (b) NH_4Cl , (c) $\text{CH}_3\text{NH}_3\text{Br}$, (d) 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 is an ion of a heavy alkaline earth metal and will therefore not affect the pH. The anion, CH_3COO^- , is the conjugate base of the weak acid CH_3COOH and will hydrolyze to produce OH^- ions, thereby making the solution basic.
- (b) In this solution, NH_4^+ is the conjugate acid of a weak base (NH_3) and is therefore acidic. Cl^- is the conjugate base of a strong acid (HCl) and therefore has no influence on the pH of the solution. Because the solution contains an ion that is acidic (NH_4^+) and one that has no influence on pH (Cl^-), the solution of NH_4Cl will be acidic.
- (c) Here CH_3NH_3^+ is the conjugate acid of a weak base (CH_3NH_2 , an amine) and is therefore acidic, and Br^- is the conjugate base of a strong acid (HBr) and therefore pH neutral. Because the solution contains one ion that is acidic and one that has no influence on pH, the solution of $\text{CH}_3\text{NH}_3\text{Br}$ will be acidic.

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

Continued

- (d) This solution contains the K^+ ion, which is a cation of group 1A, and the NO_3^- ion, which is the conjugate base of the strong acid HNO_3 . Neither of the ions will react with water to any appreciable extent, making the solution neutral.
- (e) This solution contains Al^{3+} and ClO_4^- ions. Cations, such as Al^{3+} , that have a charge of 3+ or higher are acidic. The ClO_4^- ion is the conjugate base of a strong acid (HClO_4) and therefore does not affect pH. Thus, the solution of $\text{Al}(\text{ClO}_4)_3$ will be acidic.

Practice Exercise 1

Order the following solutions from lowest to highest pH:

(i) 0.10 M NaClO, (ii) 0.10 M KBr, (iii) 0.10 M NH_4ClO_4 .

- (a) $i < ii < iii$ (b) $ii < i < iii$ (c) $iii < i < ii$
(d) $ii < iii < i$ (e) $iii < ii < i$

Practice Exercise 2

Indicate which salt in each of the following pairs forms the more acidic (or less basic) 0.010 M solution:

- (a) NaNO_3 or $\text{Fe}(\text{NO}_3)_3$, (b) KBr or KBrO ,
(c) $\text{CH}_3\text{NH}_3\text{Cl}$ or BaCl_2 , (d) NH_4NO_2 or NH_4NO_3 .

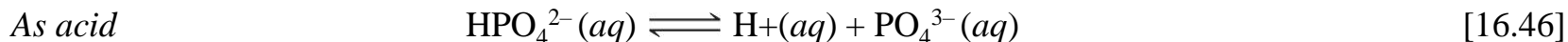
Sample Exercise 16.19 Predicting Whether the Solution of an Amphiprotic Anion Is Acidic or Basic

Predict whether the salt Na_2HPO_4 forms an acidic solution or a basic solution when dissolved in water.

Solution

Analyze We are asked to predict whether a solution of Na_2HPO_4 is acidic or basic. This substance is an ionic compound composed of Na^+ and HPO_4^{2-} ions.

Plan We need to evaluate each ion, predicting whether it is acidic or basic. Because Na^+ is a cation of group 1A, it has no influence on pH. Thus, our analysis of whether the solution is acidic or basic must focus on the behavior of the HPO_4^{2-} ion. We need to consider that HPO_4^{2-} can act as either an acid or a base:



Of these two reactions, the one with the larger equilibrium constant determines whether the solution is acidic or basic.

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

Continued

Solve The value of K_a for Equation 16.46 is K_{a3} for H_3PO_4 : 4.2×10^{-13} (Table 16.3). For Equation 16.47, we must calculate K_b for the base HPO_4^{2-} from the value of K_a for its conjugate acid, H_2PO_4^- , and the relationship $K_a \times K_b = K_w$ (Equation 16.40). The relevant value of K_a for H_2PO_4^- is K_{a2} for H_3PO_3 : 6.2×10^{-8} (from Table 16.3). We therefore have

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

$$K_b(\text{HPO}_4^{2-}) = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}.$$

This K_b value is more than 10^5 times larger than K_a for HPO_4^{2-} ; thus, the reaction in Equation 16.47 predominates over that in Equation 16.46, and the solution is basic.

TABLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$\text{HOOC}-\text{COOH}$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$\text{C}_2\text{H}_2\text{O}_2(\text{COOH})_2$	1.0×10^{-3}	4.6×10^{-5}	

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

Continued

Practice Exercise 1

How many of the following salts are expected to produce acidic solutions (see Table 16.3 for data):

NaHSO_4 , NaHC_2O_4 , NaH_2PO_4 , and NaHCO_3 ?

(a) 0 (b) 1 (c) 2 (d) 3 (e) 4

Practice Exercise 2

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

Sample Exercise 16.20 Predicting Relative Acidities from Composition and Structure

Arrange the compounds in each series in order of increasing acid strength: (a) AsH_3 , HBr , KH , H_2Se ; (b) H_2SO_4 , H_2SeO_3 , H_2SeO_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, and in (b) the substances are oxyacids.

Plan For the binary compounds, we will consider the electronegativities of As, Br, K, and Se relative to the electronegativity of H. The higher the electronegativity of these atoms, the higher the partial positive charge on H and so the more acidic the compound.

For the oxyacids, we will consider both the electronegativities of the central atom and the number of oxygen atoms bonded to the central atom.

Solve

(a) Because K is on the left side of the periodic table, it has a very low electronegativity (0.8, from Figure 8.8, p. 310). As a result, the hydrogen in KH carries a negative charge. Thus, KH should be the least acidic (most basic) compound in the series.

Arsenic and hydrogen have similar electronegativities, 2.0 and 2.1, respectively. This means that the As—H bond is nonpolar, and so AsH_3 has little tendency to donate a proton in aqueous solution.

Sample Exercise 16.20 Predicting Relative Acidities from Composition and Structure

Continued

The electronegativity of Se is 2.4, and that of Br is 2.8. Consequently, the H—Br bond is more polar than the H—Se bond, giving HBr the greater tendency to donate a proton. (This expectation is confirmed by Figure 16.19, where we see that H_2Se is a weak acid and HBr a strong acid.) Thus, the order of increasing acidity is $\text{KH} < \text{AsH}_3 < \text{H}_2\text{Se} < \text{HBr}$.

- (b) The acids H_2SO_4 and H_2SeO_4 have the same number of O atoms and the same number of OH groups. In such cases, the acid strength increases with increasing electronegativity of the central atom. Because S is slightly more electronegative than Se (2.5 vs 2.4), we predict that H_2SO_4 is more acidic than H_2SeO_4 .

For acids with the same central atom, the acidity increases as the number of oxygen atoms bonded to the central atom increases. Thus, H_2SeO_4 should be a stronger acid than H_2SeO_3 . We predict the order of increasing acidity to be $\text{H}_2\text{SeO}_3 < \text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4$.

4A	5A	6A	7A
CH₄ Neither acid nor base	NH₃ Weak base $K_b = 1.8 \times 10^{-5}$	H₂O	HF Weak acid $K_a = 6.8 \times 10^{-4}$
SiH₄ Neither acid nor base	PH₃ Very weak base $K_b = 4 \times 10^{-28}$	H₂S Weak acid $K_a = 9.5 \times 10^{-8}$	HCl Strong acid
		H₂Se Weak acid $K_a = 1.3 \times 10^{-4}$	HBr Strong acid

Increasing acid strength

Increasing acid strength

Sample Exercise 16.20 Predicting Relative Acidities from Composition and Structure

Continued

Practice Exercise 1

Arrange the following substances in order from weakest to strongest acid: HClO_3 , HOI , HBrO_2 , HClO_2 , HIO_2 .

- (a) $\text{HIO}_2 < \text{HOI} < \text{HClO}_3 < \text{HBrO}_2 < \text{HClO}_2$
- (b) $\text{HOI} < \text{HIO}_2 < \text{HBrO}_2 < \text{HClO}_2 < \text{HClO}_3$
- (c) $\text{HBrO}_2 < \text{HIO}_2 < \text{HClO}_2 < \text{HOI} < \text{HClO}_3$
- (d) $\text{HClO}_3 < \text{HClO}_2 < \text{HBrO}_2 < \text{HIO}_2 < \text{HOI}$
- (e) $\text{HOI} < \text{HClO}_2 < \text{HBrO}_2 < \text{HIO}_2 < \text{HClO}_3$

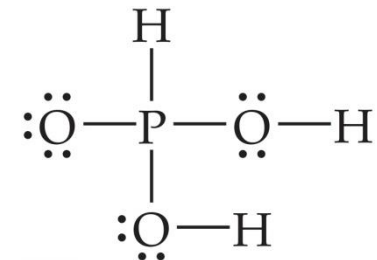
Practice Exercise 2

In each pair, choose the compound that gives the more acidic (or less basic) solution: (a) HBr , HF ; (b) PH_3 , H_2S ; (c) HNO_2 , HNO_3 ; (d) H_2SO_3 , H_2SeO_3 .

Sample Integrative Exercise Putting Concepts Together

Phosphorous acid (H_3PO_3) has the Lewis structure shown at right.

(a) Explain why H_3PO_3 is diprotic and not triprotic. (b) A 25.0-mL sample of an H_3PO_3 solution titrated with 0.102 M NaOH requires 23.3 mL of NaOH to neutralize both acidic protons. What is the molarity of the H_3PO_3 solution? (c) The original solution from part (b) has a pH of 1.59. Calculate the percent ionization and K_{a1} for H_3PO_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 H_3PO_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 percent ionization in order to compare the osmotic pressure of the two solutions in part (d).

(a) Acids have polar H—X bonds. From Figure 8.8 (p. 310) 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.

Sample Integrative Exercise Putting Concepts Together

Continued

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



From the definition of molarity, $M = \text{mol/L}$, we see that 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 H_3PO_3 . Thus, the number of moles of H_3PO_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 H_3PO_3 solution, therefore, equals $(1.19 \times 10^{-3} \text{ mol})/(0.0250 \text{ L}) = 0.0476 \text{ M}$.

Sample Integrative Exercise Putting Concepts Together

Continued

(c) From the pH of the solution, 1.59, we can calculate $[H^+]$ at equilibrium:

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

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 $H_2PO_3^-$ ion forms for each H^+ ion formed, the equilibrium concentrations of H^+ and $H_2PO_3^-$ are equal: $[H^+] = [H_2PO_3^-] = 0.026 \text{ M}$. The equilibrium concentration of H_3PO_3 equals the initial concentration minus the amount that ionizes to form H^+ and $H_2PO_3^-$: $[H_3PO_3] = 0.0476 \text{ M} - 0.026 \text{ M} = 0.022 \text{ M}$ (two significant figures). These results can be tabulated as follows:



Initial concentration (M)	0.0476	0	0
Change in concentration (M)	-0.026	+0.026	+0.026
Equilibrium concentration (M)	0.022	0.026	0.026

The percent ionization is:

$$\text{percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[H_3PO_3]_{\text{initial}}} \times 100\% = \frac{0.026 \text{ M}}{0.0476 \text{ M}} \times 100\% = 55\%$$

Sample Integrative Exercise Putting Concepts Together

Continued

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 $\text{H}^+(\text{aq})$ and 0.050 M $\text{Cl}^-(\text{aq})$, or a total of 0.100 mol/L of particles. Because H_3PO_3 is a weak acid, it ionizes to a lesser extent than HCl and, hence, there are fewer particles in the H_3PO_3 solution. As a result, the H_3PO_3 solution will have the lower osmotic pressure.