Chemistry, The Central Science, 11th edition
Theodore L. Brown, H. Eugene LeMay, Jr.,
and Bruce E. Bursten

Chapter 16
Acids and Bases

John D. Bookstaver
St. Charles Community College
Cottleville, MO

Some Definitions

- Brønsted-Lowry
  - – An acid is a proton donor.
  - – A base is a proton acceptor.

A Brønsted-Lowry acid…

…must have a removable (acidic) proton.

A Brønsted-Lowry base…

…must have a pair of nonbonding electrons.

If it can be either…

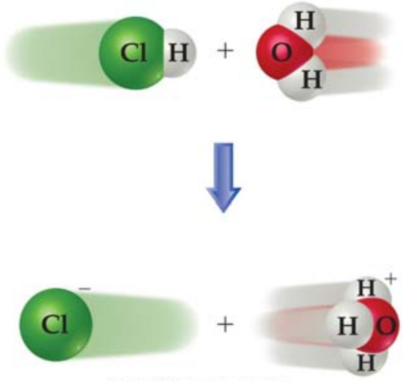
…it is amphiprotic.

HCO_3^-

HSO_4^-

H_2O

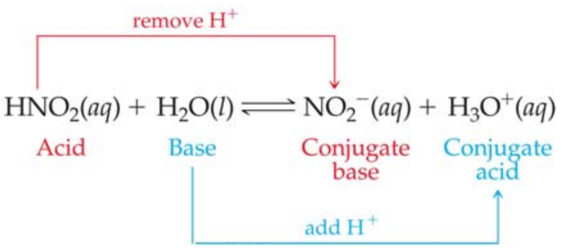
What Happens When an Acid Dissolves in Water?



- Water acts as a Brønsted-Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the conjugate base of the acid and a hydronium ion are formed.

Conjugate Acids and Bases

- The term conjugate comes from the Latin word “conjugare,” meaning “to join together.”
- Reactions between acids and bases always yield their conjugate bases and acids.



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

Sample Exercise 16.1 Identifying Conjugate Acids and Bases

(a) What is the conjugate base of each of the following acids: $HClO_4$, H_2S, PH_4^+, HCO_3^-? **(b)** What is the conjugate acid of each of the following bases: CN^-, SO_4^{2-}, H_2O, 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) $HClO_4$ less one proton (H^+) is ClO_4^-. The other conjugate bases are HS^-, PH_3, and CO_3^{2-}. **(b)** CN^- plus one proton (H^+) is HCN. 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

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

Answers: H_2SO_3, HF, HPO_4^{2-}, HCO^+

Sample Exercise 16.2 Writing Equations for Proton-Transfer Reactions

The hydrogen sulfite ion (HSO_3^-) is amphiprotic. **(a)** Write an equation for the reaction of HSO_3^- with water, in which the ion acts as an acid. **(b)** Write an equation for the reaction of 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 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: **(a)**

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$$

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). **(b)**

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq)$$

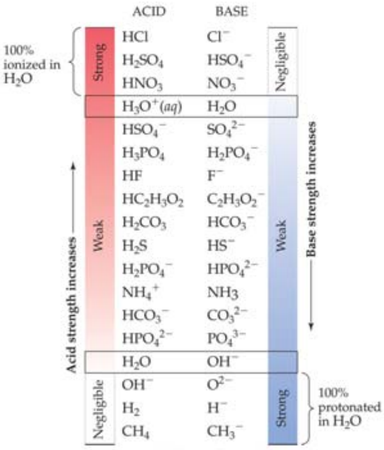
The conjugate pairs in this equation are H_2O (acid) and OH^- (conjugate base), and HSO_3^- (base) and H_2SO_3 (conjugate acid).

Practice Exercise

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 reaction that occurs, and identify the conjugate acid–base pairs.

Answer: $O^{2-}(aq) + H_2O(l) \rightarrow OH^-(aq) + OH^-(aq)$. OH^- is the conjugate acid of the base O^{2-}. OH^- is also the conjugate base of the acid H_2O.

Acid and Base Strength

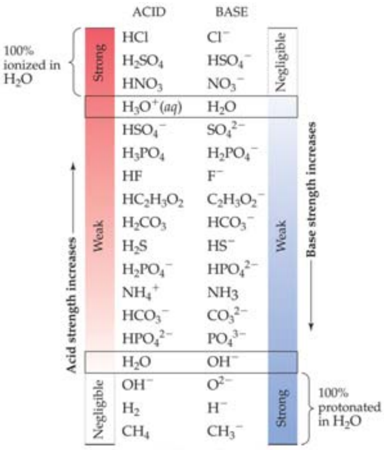


	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak	HSO_4^-	SO_4^{2-}	Weak
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible	OH^-	O^{2-}	Strong
	H_2	H^-	
	CH_4	CH_3^-	

- Strong acids are completely dissociated in water.
  - Their conjugate bases are quite weak.
- Weak acids only dissociate partially in water.
  - Their conjugate bases are weak bases.

Acids
and
Bases

Acid and Base Strength



	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak	HSO_4^-	SO_4^{2-}	Weak
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible	OH^-	O^{2-}	Strong
	H_2	H^-	
	CH_4	CH_3^-	

- Substances with negligible acidity do not dissociate in water.
  - Their conjugate bases are exceedingly strong.

Acids
and
Bases

Acid and Base Strength

- In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.

$$HCl\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

- H_2O is a much stronger base than Cl^-, so the equilibrium lies so far to the right that K is not measured (K>>1).

Acid and Base Strength

- In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.

$$CH_3CO_2H\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3CO_2^-\ (aq)$$

- Acetate is a stronger base than H_2O, so the equilibrium favors the left side (K<1).

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 ($K_c > 1$):

$$HSO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HCO_3^-(aq)$$

Solution

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 CO_3^{2-}, the base in the forward reaction as written, 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.

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

$$\underset{\text{Acid}}{HSO_4^-(aq)} + \underset{\text{Base}}{CO_3^{2-}(aq)} \rightleftharpoons \underset{\text{Conjugate base}}{SO_4^{2-}(aq)} + \underset{\text{Conjugate acid}}{HCO_3^-(aq)} \qquad K_c > 1$$

Comment: Of the two acids in the equation, HSO_4^- and 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:

(a) $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$

(b) $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$

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

Autoionization of Water

- As we have seen, water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.

$$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

- This is referred to as autoionization.

Ion-Product Constant

- The equilibrium expression for this process is

$$K_c = [H_3O^+] [OH^-]$$

- This special equilibrium constant is referred to as the **ion-product constant** for water, K_w.
- At 25°C, $K_w = 1.0 \times 10^{-14}$

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

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

Solution

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

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

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

Practice Exercise

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:
(a) [H$^+$] = 4×10^{-9} *M* ; **(b)** [H$^+$] = 4×10^{-9} *M* ; **(c)** [OH$^–$] = 7×10^{-13} *M* .
Answers: **(a)** basic, **(b)** neutral, **(c)** acidic

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 1.8×10^{-9} *M* .

Note: In this problem and all that follow, we assume, unless stated otherwise, that the temperature is 25 ºC.

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:

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

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

This solution is basic because

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

(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

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)** 5×10^{-9} *M*, **(b)** 1.0×10^{-7} *M*, **(c)** 1.0×10^{-8} *M*

---

pH

pH is defined as the negative base-10 logarithm of the concentration of hydronium ion.

$$pH = -\log [H_3O^+]$$

pH

- In pure water,

$$K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$$

- Since in pure water $[H_3O^+] = [OH^-]$,

$$[H_3O^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

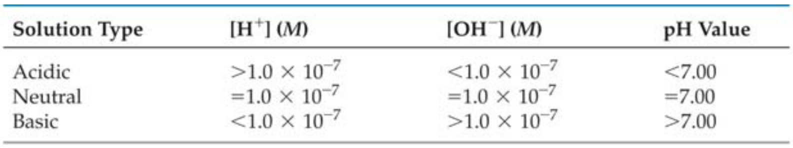
---

pH

- Therefore, in pure water,

$$pH = -\log (1.0 \times 10^{-7}) = 7.00$$

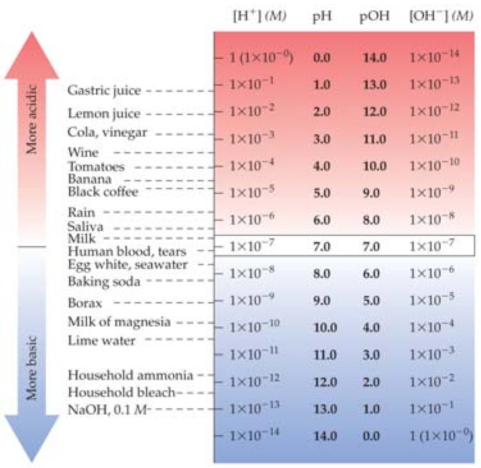
- An acid has a higher $[H_3O^+]$ than pure water, so its pH is <7.
- A base has a lower $[H_3O^+]$ than pure water, so its pH is >7.



Solution Type	$[H^+]$ (*M*)	$[OH^-]$ (*M*)	pH Value
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	$=7.00$
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

pH

These are the pH values for several common substances.



$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*M*)
1 (1×10^{-0})	0.0	14.0	1×10^{-14}
1×10^{-1}	1.0	13.0	1×10^{-13}
1×10^{-2}	2.0	12.0	1×10^{-12}
1×10^{-3}	3.0	11.0	1×10^{-11}
1×10^{-4}	4.0	10.0	1×10^{-10}
1×10^{-5}	5.0	9.0	1×10^{-9}
1×10^{-6}	6.0	8.0	1×10^{-8}
1×10^{-7}	7.0	7.0	1×10^{-7}
1×10^{-8}	8.0	6.0	1×10^{-6}
1×10^{-9}	9.0	5.0	1×10^{-5}
1×10^{-10}	10.0	4.0	1×10^{-4}
1×10^{-11}	11.0	3.0	1×10^{-3}
1×10^{-12}	12.0	2.0	1×10^{-2}
1×10^{-13}	13.0	1.0	1×10^{-1}
1×10^{-14}	14.0	0.0	1 (1×10^{-0})

Other “p” Scales

- The “p” in pH tells us to take the negative base-10 logarithm of the quantity (in this case, hydronium ions).
- Some similar examples are
  - pOH: -log $[OH^-]$
  - pK_w: -log K_w

Watch This!

Because

$$[H_3O^+]\,[OH^-] = K_w = 1.0 \times 10^{-14},$$

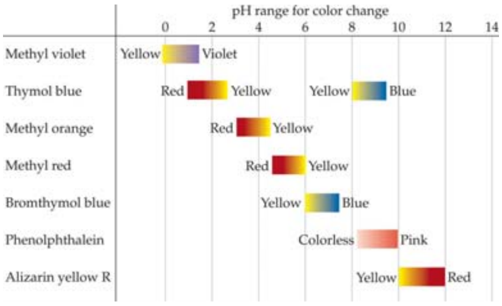
we know that

$$-\log\,[H_3O^+] + -\log\,[OH^-] = -\log K_w = 14.00$$

or, in other words,

$$pH + pOH = pK_w = 14.00$$

How Do We Measure pH?



- For less accurate measurements, one can use
  - Litmus paper
    - “Red” paper turns blue above ~pH = 8
    - “Blue” paper turns red below ~pH = 5
  - Or an indicator.

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 ×10^{-12} *M*.

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

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 × 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}

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

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 × 10^{-4} *M*. What is the pH? **(b)** A commonly available window-cleaning solution has [OH$^-$] = 1.9 ×10^{-6} *M* . What is the pH?
***Answers:* (a)** 3.42, **(b)** [H$^+$] = 5.3 ×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

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

Thus,

$$\log[\text{H}^+] = -3.76$$

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:

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

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 × 10^{-3} and 1 × 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× 10^{-10} *M*

How Do We Measure pH?

For more accurate measurements, one uses a pH meter, which measures the voltage in the solution.

Strong Acids

- You will recall that the seven strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.
- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.
- For the monoprotic strong acids,

$$[H_3O^+] = [acid].$$

Strong Bases

- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca^{2+}, Sr^{2+}, and Ba^{2+}).
- Again, these substances dissociate completely in aqueous solution.

Sample Exercise 16.8 Calculating the pH of a Strong Acid

What is the pH of a 0.040 *M* solution of $HClO_4$?

Solution

Analyze and Plan: Because $HClO_4$ is a strong acid, it is completely ionized, giving $[H^+] = [ClO_4^-] = 0.040\ M$
Solve: The pH of the solution is given by

$$pH = -\log(0.040) = 1.40.$$

Check: Because $[H^+]$ 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

An aqueous solution of HNO_3 has a pH of 2.34. What is the concentration of the acid?
Answer: 0.0046 *M*

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:

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

Method 2:

$$pOH = -\log(0.028) = 1.55 \qquad pH = 14.00 - pOH = 12.45$$

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

Method 1:

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

Method 2:

$$pOH = -\log(0.0022) = 2.66 \qquad pH = 14.00 - pOH = 11.34$$

Practice Exercise

What is the concentration of a solution of **(a)** KOH for which the pH is 11.89; **(b)** $Ca(OH)_2$ for which the pH is 11.68?

Answers: **(a)** 7.8×10^{-3} *M*, **(b)** 2.4×10^{-3} *M*

Dissociation Constants

- For a generalized acid dissociation,

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons A^-\ (aq) + H_3O^+\ (aq)$$

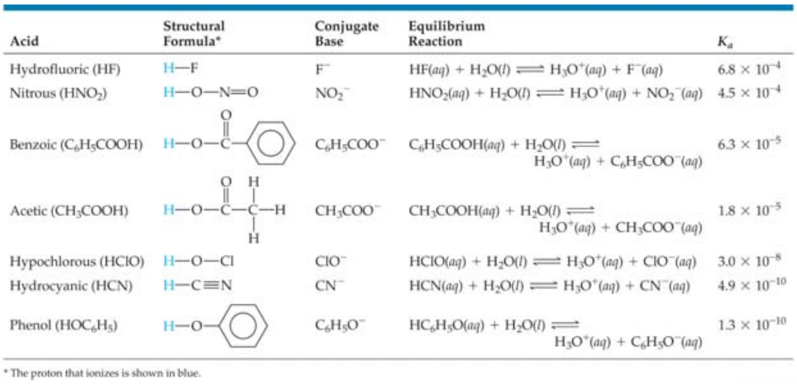
  the equilibrium expression would be

$$K_c = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

- This equilibrium constant is called the acid-dissociation constant, K_a.

Dissociation Constants

The greater the value of K_a, the stronger is the acid.



Acid	Structural Formula*	Conjugate Base	Equilibrium Reaction	K_a
Hydrofluoric (HF)	$H-F$	F^-	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	6.8×10^{-4}
Nitrous (HNO_2)	$H-O-N=O$	NO_2^-	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
Benzoic (C_6H_5COOH)	$H-O-\overset{O}{\overset{\|}{C}}-C_6H_5$	$C_6H_5COO^-$	$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5COO^-(aq)$	6.3×10^{-5}
Acetic (CH_3COOH)	$H-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{\vert}{\underset{H}{\underset{\vert}{C}}}}-H$	CH_3COO^-	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$	1.8×10^{-5}
Hypochlorous (HClO)	$H-O-Cl$	ClO^-	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	3.0×10^{-8}
Hydrocyanic (HCN)	$H-C\equiv N$	CN^-	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol (HOC_6H_5)	$H-O-C_6H_5$	$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

* The proton that ionizes is shown in blue.

Calculating K_a from the pH

The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

We know that

$$K_a = \frac{[H_3O^+]\,[COO^-]}{[HCOOH]}$$

Calculating K_a from the pH

The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

To calculate K_a, we need the equilibrium concentrations of all three things.

We can find $[H_3O^+]$, which is the same as $[HCOO^-]$, from the pH.

Calculating K_a from the pH

$$\mathrm{pH} = -\log\,[H_3O^+]$$
$$2.38 = -\log\,[H_3O^+]$$
$$-2.38 = \log\,[H_3O^+]$$
$$10^{-2.38} = 10^{\log\,[H_3O^+]} = [H_3O^+]$$
$$4.2 \times 10^{-3} = [H_3O^+] = [HCOO^-]$$

Calculating K_a from pH

Now we can set up a table…

	[HCOOH], *M*	$[H_3O^+]$, *M*	$[HCOO^-]$, *M*
Initially	0.10	0	0
Change			
At Equilibrium			

Calculating K_a from pH

$$K_a = \frac{[4.2 \times 10^{-3}]\ [4.2 \times 10^{-3}]}{[0.10]}$$

$$= 1.8 \times 10^{-4}$$

Sample Exercise 16.10 Calculating K_a from Measured pH

A student prepared a 0.10 *M* solution of formic acid (HCOOH) and measured its pH. The pH at 25 ºC 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:

$$HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$$

The equilibrium-constant expression is

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

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

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

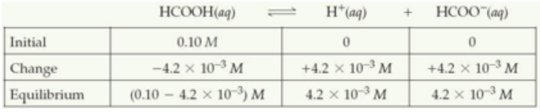
$$\log[H^+] = -2.38$$

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

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 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 ion HCOO$^-$ are produced in solution. Because the pH measurement indicates that [H$^+$] = 4.2 × 10^{-3} *M* at equilibrium, we can construct the following table:

Sample Exercise 16.10 Calculating K_a from Measured pH

Solution (Continued)



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

Notice that we have neglected the very small concentration of H$^+$(*aq*) that is due to the autoionization of H_2O. 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*:

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

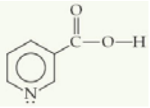
We can now insert the equilibrium centrations into the expression for K_a:

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

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 *M* solution of niacin has a pH of 3.26. What is the acid-dissociation constant, K_a, for niacin?

Answers: 1.5 × 10^{-5}

Calculating Percent Ionization

- Percent Ionization = $\dfrac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100$
- In this example

$$[H_3O^+]_{eq} = 4.2 \times 10^{-3}\ M$$

$$[HCOOH]_{initial} = 0.10\ M$$

$$\text{Percent Ionization} = \frac{4.2 \times 10^{-3}}{0.10} \times 100$$

$$= 4.2\%$$

Acids and Bases

Sample Exercise 16.11 Calculating Percent Ionization

A 0.10 *M* solution of formic acid (HCOOH) contains 4.2 × 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%

Acids and Bases

Calculating pH from K_a

Calculate the pH of a 0.30 M solution of acetic acid, $HC_2H_3O_2$, at 25°C.

$$HC_2H_3O_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_2H_3O_2^-\ (aq)$$

K_a for acetic acid at 25°C is 1.8×10^{-5}.

Calculating pH from K_a

The equilibrium constant expression is

$$K_a = \frac{[H_3O^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Calculating pH from K_a

We next set up a table…

	$[C_2H_3O_2]$, *M*	$[H_3O^+]$, *M*	$[C_2H_3O_2^-]$, *M*
Initially	0.30	0	0
Change			
At Equilibrium			

We are assuming that x will be very small compared to 0.30 and can, therefore, be ignored.

Calculating pH from K_a

Now,

$$1.8 \times 10^{-5} = \frac{(x)^2}{(0.30)}$$

$$(1.8 \times 10^{-5})\ (0.30) = x^2$$

$$5.4 \times 10^{-6} = x^2$$

$$2.3 \times 10^{-3} = x$$

Calculating pH from K_a

$$\begin{aligned} pH &= -\log [H_3O^+] \\ &= -\log (2.3 \times 10^{-3}) \\ &= 2.64 \end{aligned}$$

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, *Ka* for HCN is 4.9×10^{-10}.

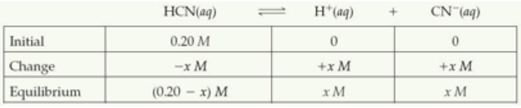
Plan: We proceed as in the example just worked in the text, writing the chemical equation and constructing a table of initial and equilibrium concentrations in which the equilibrium concentration of H^+ is our unknown.

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

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

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

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



	$HCN(aq)$	$\rightleftharpoons$ $H^+(aq)$	+ $CN^-(aq)$
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,

$$0.20 - x \simeq 0.20$$

Thus,

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

Solving for *x*, we have

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

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

A concentration of 9.9 × 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:

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

Practice Exercise

The *Ka* for niacin (Practice Exercise 16.10) is 1.5 × 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.

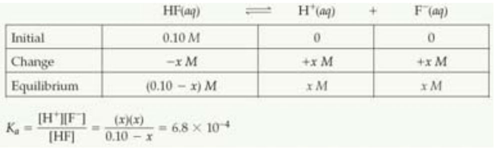
Solution

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 × 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:



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

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

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

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

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

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

This equation can be solved using the standard quadratic formula.

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

Substituting the appropriate numbers gives

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

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

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

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

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

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

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

Solving the resultant quadratic expression, we obtain

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

The percentage of molecules ionized is

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

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

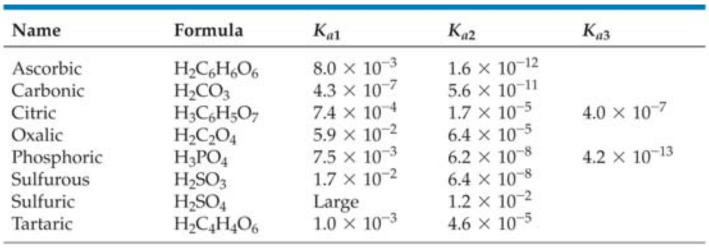
In Practice Exercise 16.11, we found that the percent ionization of niacin ($K_a = 1.5 \times 10^{-5}$) in a 0.020 *M* solution is 2.7%. Calculate the percentage of niacin molecules ionized in a solution that is **(a)** 0.010 *M*, **(b)** 1.0×10^{-3} *M*.

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

Polyprotic Acids…

…have more than one acidic proton

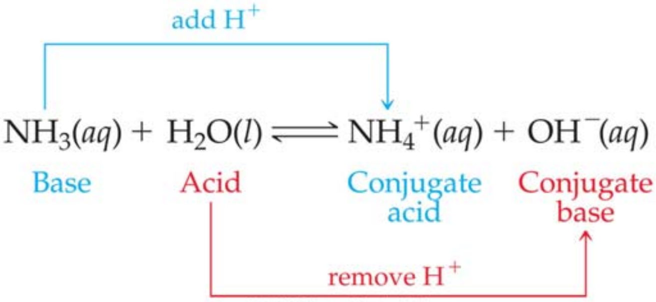
If the difference between the K_a for the first dissociation and subsequent K_a values is 10^3 or more, the pH generally depends *only* on the first dissociation.



Name	**Formula**	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-3}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	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	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

Weak Bases

Bases react with water to produce hydroxide ion.



$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Weak Bases

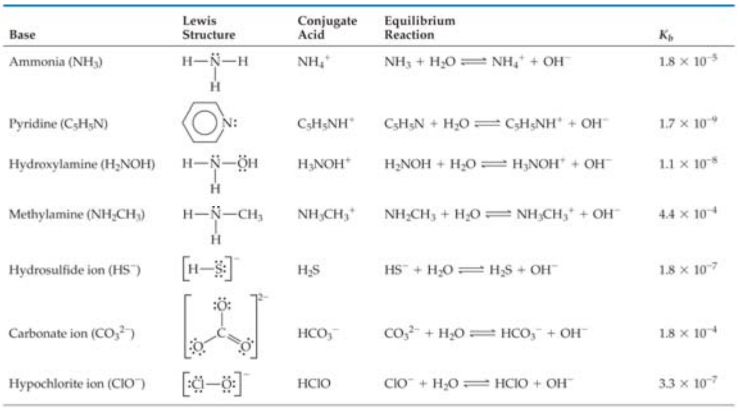
The equilibrium constant expression for this reaction is

$$K_b = \frac{[HB]\,[OH^-]}{[B^-]}$$

where K_b is the base-dissociation constant.

Weak Bases

K_b can be used to find [OH^-] and, through it, pH.



Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	K_b
Ammonia (NH_3)	H—N̈—H H	NH_4^+	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C_5H_5N)	N:	$C_5H_5NH^+$	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)	H—N̈—ÖH H	H_3NOH^+	$H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)	H—N̈—CH_3 H	$NH_3CH_3^+$	$NH_2CH_3 + H_2O \rightleftharpoons NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	[H—S̈:]$^-$	H_2S	$HS^- + H_2O \rightleftharpoons H_2S + OH^-$	1.8×10^{-7}
Carbonate ion (CO_3^{2-})	[:Ö: C :Ö: Ö:]$^{2-}$	HCO_3^-	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	1.8×10^{-4}
Hypochlorite ion (ClO^-)	[:C̈l—Ö:]$^-$	HClO	$ClO^- + H_2O \rightleftharpoons HClO + OH^-$	3.3×10^{-7}

Sample Exercise 16.15 Using K_b to Calculate 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 are 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, 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:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

We then tabulate the equilibrium concentrations involved in the equilibrium:

	$NH_3(aq)$	+ $H_2O(l)$	$\rightleftharpoons$ $NH_4^+(aq)$	+ $OH^-(aq)$
Initial	0.15 *M*	—	0	0
Change	$-x$ *M*	—	$+x$ *M*	$+x$ *M*
Equilibrium	$(0.15 - x)$ *M*	—	x *M*	x *M*

(We ignore the concentration of H_2O because it is not involved in the equilibrium-constant expression.) Inserting these quantities into the equilibrium-constant expression gives the following:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{0.15 - x} = 1.8 \times 10^{-5}$$

Because K_b is small, we can neglect the small amount of NH_3 that reacts with water, as compared to the total NH_3 concentration; that is, we can neglect x relative to 0.15 *M*. Then we have

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

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

$$x = [NH_4^+] = [OH^-] = \sqrt{2.7 \times 10^{-6}} = 1.6 \times 10^{-3}\,M$$

Sample Exercise 16.15 Using K_b to Calculate OH^{-}

Solution (Continued)

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 [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 [OH^{-}] = 1.6×10^{-3} *M*. Thus, pOH = $-\log(1.6 \times 10^{-3}) = 2.80$, and 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 Na^+ and ClO^- ions. As such, it is a strong electrolyte that completely dissociates in solution into Na^+, which is a spectator ion, and 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 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 $[ClO^-]$ using the equilibriumconstant expression, K_b.

Solve:

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

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

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.

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

	$ClO^-(aq)$	$H_2O(l)$	$HClO(aq)$	$OH^-(aq)$
Initial	$x\ M$	—	0	0
Change	$-3.2 \times 10^{-4}\ M$	—	$+3.2 \times 10^{-4}\ M$	$+3.2 \times 10^{-4}\ M$
Equilibrium	$(x - 3.2 \times 10^{-4})\ M$	—	$3.2 \times 10^{-4}\ M$	$3.2 \times 10^{-4}\ M$

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:

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

Thus

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

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

A solution of NH_3 in water has a pH of 11.17. What is the molarity of the solution?
Answer: 0.12 *M*

pH of Basic Solutions

What is the pH of a 0.15 *M* solution of NH_3?

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

---

pH of Basic Solutions

Tabulate the data.

	$[NH_3]$, *M*	$[NH_4^+]$, *M*	$[OH^-]$, *M*
Initially	0.15	0	0
At Equilibrium			

pH of Basic Solutions

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

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

$$2.7 \times 10^{-6} = x^2$$

$$1.6 \times 10^{-3} = x$$

Acids
and
Bases

---

pH of Basic Solutions

Therefore,

$[OH^-] = 1.6 \times 10^{-3}$ M

$pOH = -\log(1.6 \times 10^{-3})$

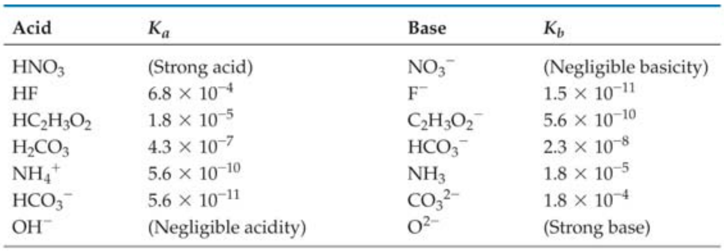
$= 2.80$

$pH = 14.00 - 2.80$

$= 11.20$

Acids
and
Bases

K_a and K_b



Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	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)

K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

Therefore, if you know one of them, you can calculate the other.

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 aciddissociation 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^-:

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

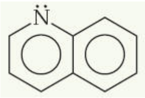
(b) K_b for NH_3 is listed in Table 16.4 and in Appendix D as $K_b = 1.8 \times 10^{-5}$. Using Equation 16.40, we can calculate K_a for the conjugate acid, NH_4^+ :

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

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: NO_2^-, PO_4^{3-}, or N_3^-? **(b)** The base quinoline has the following structure:



Its conjugate acid is listed in handbooks as having a pK_a of 4.90. What is the base dissociation constant for quinoline?

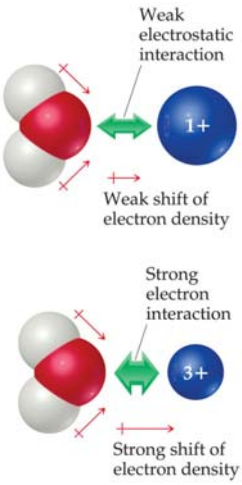
Answers: **(a)** PO_4^{3-} ($K_b = 2.4 \times 10^{-2}$), **(b)** 7.9×10^{-10}

Reactions of Anions with Water

- Anions are bases.
- As such, they can react with water in a hydrolysis reaction to form OH^- and the conjugate acid:

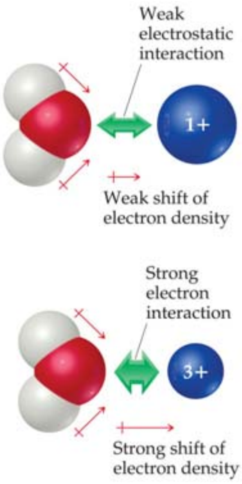
$$X^- (aq) + H_2O (l) \rightleftharpoons HX (aq) + OH^- (aq)$$

Reactions of Cations with Water



- Cations with acidic protons (like NH_4^+) will lower the pH of a solution.
- Most metal cations that are hydrated in solution also lower the pH of the solution.

Reactions of Cations with Water



- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O-H bond more polar and the water more acidic.
- Greater charge and smaller size make a cation more acidic.

Effect of Cations and Anions

1. An anion that is the conjugate base of a strong acid will not affect the pH.
2. An anion that is the conjugate base of a weak acid will increase the pH.
3. A cation that is the conjugate acid of a weak base will decrease the pH.

Effect of Cations and Anions

4. Cations of the strong Arrhenius bases will not affect the pH.
5. Other metal ions will cause a decrease in pH.
6. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the K_a and K_b values.

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)** $Ba(CH_3COO)_2$, **(b)** NH_4Cl, **(c)** CH_3NH_3Br, **(d)** KNO_3, **(e)** $Al(ClO_4)_3$.

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, 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, CH_3COO^-, is the conjugate base of the weak acid CH_3COOH and will hydrolyze to produce OH^- ions, thereby making the solution basic (summary point 2).

(b) This solution contains NH_4^+ and Cl^- ions. NH_4^+ is the conjugate acid of a weak base (NH_3) and is therefore acidic (summary point 3). Cl^- is the conjugate base of a strong acid (HCl) and therefore has no influence on the pH of the solution (summary point 1). 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) This solution contains $CH_3NH_3^+$ and Br^- ions. $CH_3NH_3^+$ is the conjugate acid of a weak base (CH_3NH_2, an amine) and is therefore acidic (summary point 3). is the conjugate base of a strong acid (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 CH_3NH_3Br will be acidic.

(d) This solution contains the K^+ ion, which is a cation of group 1A, and the ion NO_3^-, which is the conjugate base of the strong acid HNO_3. Neither of the ions will react with water to any appreciable extent (summary points 1 and 4), making the solution neutral.

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

Solution (Continued)

(e) This solution contains Al^{3+} and ClO_4^- ions. Cations, such as Al^{3+}, that are not in groups 1A or 2A are acidic (summary point 5). The ClO_4^- ion is the conjugate base of a strong acid ($HClO_4$) and therefore does not affect pH (summary point 1). Thus, the solution of $Al(ClO_4)_3$ 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)** $NaNO_3$, or $Fe(NO_3)_3$; **(b)** KBr, or KBrO; **(c)** CH_3NH_3Cl, or $BaCl_2$, **(d)** NH_4NO_2, or NH_4NO_3.

Answers: **(a)** $Fe(NO_3)_3$, **(b)** KBr, **(c)** CH_3NH_3Cl, **(d)** NH_4NO3

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

Predict whether the salt Na_2HPO_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 Na_2HPO_4 will be 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 each is acidic or basic. Because 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 HPO_4^{2-} ion. We need to consider the fact that HPO_4^{2-} can act as either an acid or a base.

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad [16.45]$$

$$HPO_4^{2-}(aq) + H_2O \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq) \qquad [16.46]$$

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 4.2×10^{-13} . We must calculate the value of K_b for Equation 16.46 from the value of K_a for its conjugate acid, $H_2PO_4^-$. 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 HPO_4^{2-}, knowing the value of K_a for the conjugate acid HPO_4^{2-}:

$$K_b(HPO_4^{2-}) \times K_a(H_2PO_4^-) = K_w = 1.0 \times 10^{-14}$$

Because K_a for $H_2PO_4^-$ is 6.2×10^{-8} (Table 16.3), we calculate K_b for $H_2PO_4^{2-}$ to be 1.6×10^{-7}. This is more than 10^5 times larger than K_a for $H_2PO_4^{2-}$; thus, the reaction shown in Equation 16.46 predominates over that in Equation 16.45, and the solution will be basic.

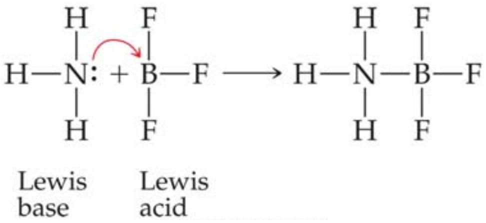
Sample Exercise 16.19 Predicting Whether the Solution of an Amphiprotic Anion is Acidic or Basic

Practice Exercise

Predict whether the dipotassium salt of citric acid ($K_2HC_6H_5O_7$) will form an acidic or basic solution in water (see Table 16.3 for data).

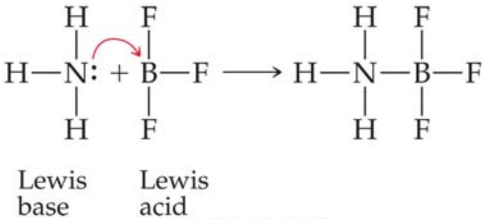
Answer: acidic

Lewis Acids



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.

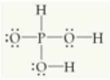
Lewis Bases



- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted-Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.

Sample Integrated Exercise Putting Concepts Together

Phosphorous acid (H_3PO_3) has the following Lewis structure



(a) Explain why H_3PO_3 is diprotic and not triprotic. **(b)** A 25.0-mL sample of a solution of H_3PO_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 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 $K_{a1} >> K_{a2}$. **(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 $[H^+]$ 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

$$H_3PO_3(aq) + 2\ NaOH(aq) \rightarrow Na_2HPO3(aq) + 2\ H_2O(l)$$

Sample Integrated Exercise Putting Concepts Together

Solution (Continued)

From the definition of molarity, *M* = mol/L, we see that moles = *M* × L. (Section 4.5) Thus, the number of moles of NaOH added to the solution is (0.0233 L)(0.102 mol/L) = 2.38×10^{-3} 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

$$(2.38 \times 10^{-3}\ \text{mol NaOH})\left(\frac{1\ \text{mol}\ H_3PO_3}{2\ \text{mol NaOH}}\right) = 1.19 \times 10^{-3}\ \text{mol}\ H_3PO_3$$

The concentration of the H_3PO_3 solution, therefore, equals (1.19×10^{-3} mol)/(0.0250 L) = 0.0476 *M*.

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

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

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

$$H_3PO_3(aq) \rightleftharpoons H^+(aq) + H_2PO_3^-(aq)$$

Because one $H_2PO_3^-$ ion forms for each H^+ ion formed, the equilibrium concentrations of H^+ and $H_2PO_3^-$ are equal: $[H^+] = [H_2PO3^-]$ = 0.026 *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 *M* – 0.026 *M* = 0.022 *M* (two significant figures). These results can be tabulated as follows:

	$H_3PO_3(aq)$	$\rightleftharpoons$ $H^+(aq)$	+ $H_2PO_3^-(aq)$
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*

Sample Integrated Exercise Putting Concepts Together

Solution (Continued)

The percent ionization is

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

The first acid-dissociation constant is

$$K_{a1} = \frac{[H^+][H_2PO_3^-]}{[H_3PO_3]} = \frac{(0.026)(0.026)}{0.022} = 0.031$$

(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* $H^+(aq)$ and 0.050 *M* $Cl^-(aq)$, 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.