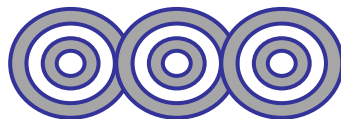




**Chemistry, The Central Science, 11th edition**  
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# Chapter 16

## Acid-Base Equilibria

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Acids and bases are important in numerous chemical processes that occur around us – from industrial processes to biological ones, from reactions in the laboratory to those in our environment.

The time required for a metal object immersed in water to corrode, the ability of an aquatic environment to support fish and plant life, the fate of pollutants washed out of the air by rain, and even the rates of reactions that maintain our lives all critically depend upon the acidity or basicity of solutions.

Indeed, an enormous amount of chemistry can be understood in terms of acid-base reactions.

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# **16.1**

## **Acids and Bases: A Brief Review**

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# Arrhenius Definition

An **acid** is a substance that, when dissolved in water, increases the concentration of hydrogen ions ( $\text{H}^+$ ).



A **base** is a substance that, when dissolved in water, increases the concentration of hydroxide ions ( $\text{OH}^-$ ).



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# **16.2**

# **Brønsted-Lowry Acids and Bases**

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# Brønsted-Lowry Definition

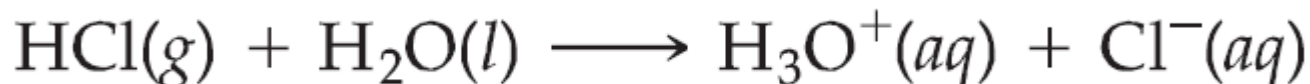
The Arrhenius concept of acids and bases, while useful, has limitations. For one thing, it is restricted to aqueous solutions.

Brønsted-Lowry concept is based on the fact that acid-base reactions involve the transfer of  $\text{H}^+$  ions from one substance to another.

## Brønsted-Lowry

An acid is a proton donor.

A base is a proton acceptor.



When a proton is transferred from HCl to  $\text{H}_2\text{O}$ , HCl acts as the Brønsted-Lowry acid and  $\text{H}_2\text{O}$  acts as the Brønsted-Lowry base.

## What happens when an acid dissolves in water?

Water acts as a Brønsted-Lowry base and abstracts a proton ( $\text{H}^+$ ) from the acid.

As a result, the **conjugate base** of the acid and a **hydronium ion** are formed.

An  $\text{H}^+$  ion is simply a proton with no surrounding valence electron. This small, positively charged particle interacts strongly with the nonbonding electron pairs.

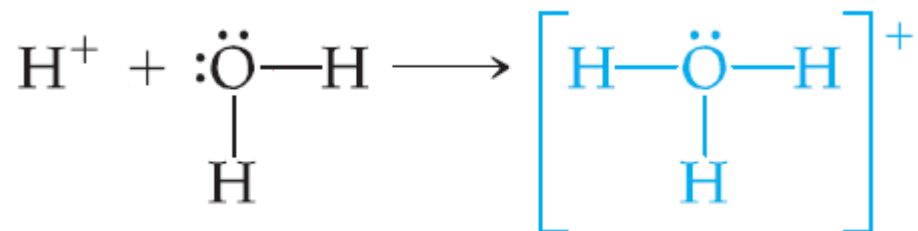
**A Brønsted-Lowry acid...**

...must have a removable (acidic) proton

**A Brønsted-Lowry base...**

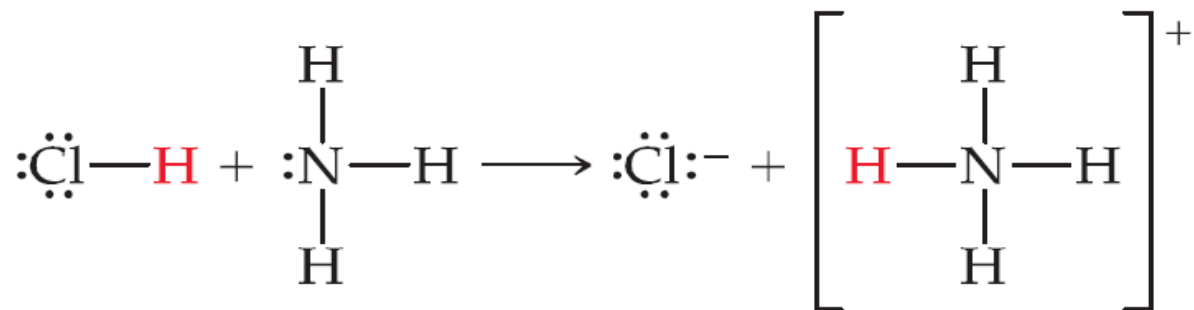
...must have a pair of nonbonding electrons

Water molecules to form hydrated hydrogen ions. For example, the interaction of a proton with one water molecule forms the hydronium ion,  $\text{H}_3\text{O}^+(\text{aq})$



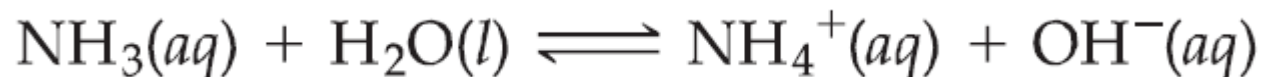
Chemists use  $\text{H}^+(\text{aq})$  and  $\text{H}_3\text{O}^+(\text{aq})$  interchangeably to represent the same thing – namely the hydrated proton that is responsible for the characteristic properties of aqueous solutions of acids.

Because the emphasis in the Brønsted-Lowry concept is on proton transfer, the concept also applies to reactions that do not occur in aqueous solution. In the reaction between  $\text{HCl}$  and  $\text{NH}_3$ , for example, a proton is transferred from the acid  $\text{HCl}$  to the base  $\text{NH}_3$ .





Ammonia is an Arrhenius base because adding it to water leads to an increase in the concentration of  $\text{OH}^-(\text{aq})$ . It is a Brønsted-Lowry base because it accepts a proton from  $\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  molecule in the equation acts as a Brønsted-Lowry acid because it donates a proton to the  $\text{NH}_3$  molecule.



An acid and a base always work together to transfer a proton. In other words, a substance can function as an acid only if another substance simultaneously behaves as a base.

- To be a Brønsted-Lowry acid, a molecule or ion must have a hydrogen atom that it can lose as an  $\text{H}^+$  ion.
- To be a Brønsted-Lowry base, a molecule or ion must have a nonbonding pair of electrons that it can use to bind the  $\text{H}^+$  ion.

Some substances can act as an acid in one reaction and as a base in another.

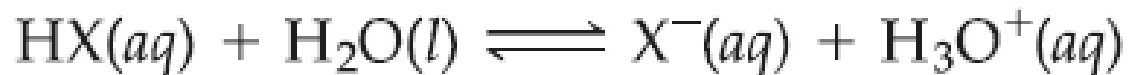
For example,  $\text{H}_2\text{O}$  is a Brønsted-Lowry base in its reaction with  $\text{HCl}$  and a Brønsted-Lowry acid in its reaction with  $\text{NH}_3$ .

A substance that is capable of acting as either an acid or a base is called **amphiprotic**.

An amphiprotic substance acts as a base when combined with something more strongly acidic than itself and an acid when combined with something more strongly basic than itself.

**e.g.,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{H}_2\text{O}$**

# Conjugate Acids and Bases

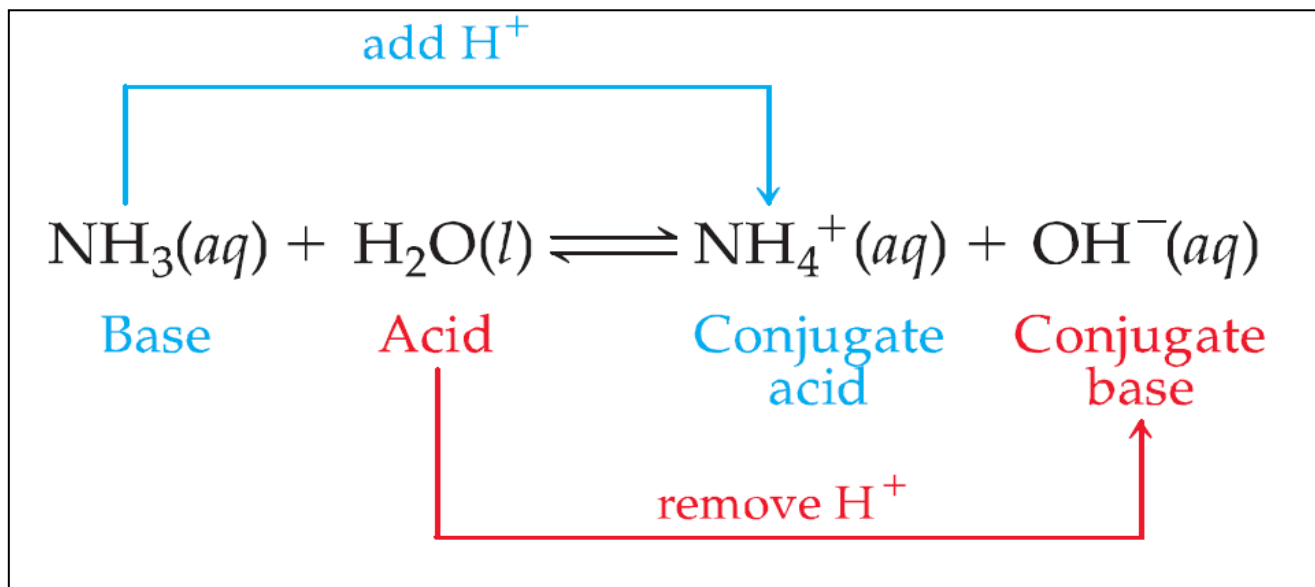
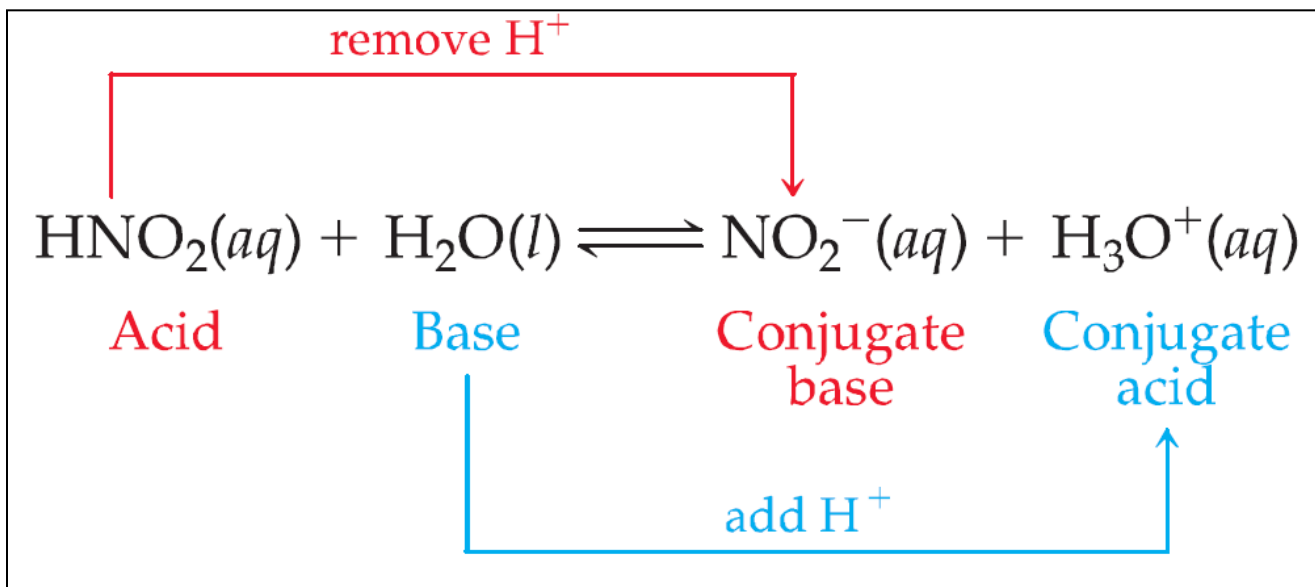


In the forward reaction HX donates a proton to H<sub>2</sub>O. Therefore, HX is the Brønsted-Lowry acid, and H<sub>2</sub>O is the Brønsted-Lowry base. In the reverse reaction the H<sub>3</sub>O<sup>+</sup> ion donates a proton to the X<sup>-</sup> ion, so H<sub>3</sub>O<sup>+</sup> is the acid and X<sup>-</sup> is the base. When the acid HX donates a proton, it leaves X<sup>-</sup> which can act as a base. Likewise, when H<sub>2</sub>O acts as a base, it generates H<sub>3</sub>O<sup>+</sup>, which can act as an acid.

An acid and a base such as HX and X<sup>-</sup> that differ only in the presence or absence of a proton are called a **conjugate acid-base pair**.

-Every acid has a conjugate base, formed by removing a proton from the acid, for example, OH<sup>-</sup> is the conjugate base of H<sub>2</sub>O, and X<sup>-</sup> is the conjugate base of HX.

-Every base has associated with it a conjugate acid, formed by adding a proton to the base. Thus, H<sub>3</sub>O<sup>+</sup> is the conjugate acid of H<sub>2</sub>O, and HX is the conjugate acid of X<sup>-</sup>.



## Sample Exercise 16.1 Identifying Conjugate Acids and Bases

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

### Solution

(a)  $\text{HClO}_4$  less one proton ( $\text{H}^+$ ) is  $\text{ClO}_4^-$ . The other conjugate bases are  $\text{HS}^-$ ,  $\text{PH}_3$ , and  $\text{CO}_3^{2-}$ .

(b)  $\text{CN}^-$  plus one proton ( $\text{H}^+$ ) is  $\text{HCN}$ . The other conjugate acids are  $\text{HSO}_4^-$ ,  $\text{H}_3\text{O}^+$ , and  $\text{H}_2\text{CO}_3$ .

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

### Practice Exercise

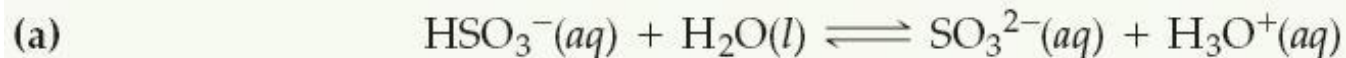
Write the formula for the conjugate acid of each of the following:  $\text{HSO}_3^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}$ .

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

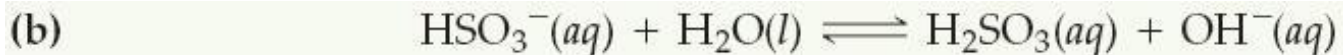
## Sample Exercise 16.2 Writing Equations for Proton-Transfer Reactions

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

### Solution



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



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

# Acid and Base Strength

	ACID	BASE		
100% ionized in H <sub>2</sub> O	Strong	HCl	Cl <sup>-</sup>	Negligible
		H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	
		HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	
		H <sub>3</sub> O <sup>+</sup> (aq)	H <sub>2</sub> O	
Acid strength increases ↑	Weak	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Weak
		H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	
		HF	F <sup>-</sup>	
		HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
		H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	
		H <sub>2</sub> S	HS <sup>-</sup>	
		H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	
		NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	
		HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	
		HPO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	
			H <sub>2</sub> O	
Negligible		OH <sup>-</sup>	O <sup>2-</sup>	Strong
		H <sub>2</sub>	H <sup>-</sup>	
		CH <sub>4</sub>	CH <sub>3</sub> <sup>-</sup>	
				100% protonated in H <sub>2</sub> O

Base strength increases ↓

**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.

**Substances with negligible acidity do not dissociate in water.**

Their conjugate bases are exceedingly strong.

**Example:**

CH<sub>4</sub> contains hydrogen but does not demonstrate any acidic behavior in water. Its conjugate base (CH<sub>3</sub><sup>-</sup>) is a strong base.

- The stronger an acid, the weaker is its conjugate base.
- The stronger a base, the weaker is its conjugate acid.

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



$\text{H}_2\text{O}$  is a much stronger base than  $\text{Cl}^-$ , so the equilibrium lies so far to the right that  $K$  is not measured ( $K \gg 1$ ).



Acetate  $\text{CH}_3\text{COO}^-$  is a stronger base than  $\text{H}_2\text{O}$ , so the equilibrium favors the left side ( $K < 1$ ).



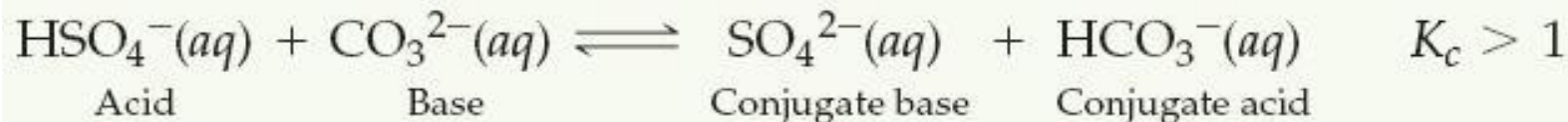
## Sample Exercise 16.3 Predicting the Position of a Proton-Transfer Equilibrium

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



### Solution

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



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

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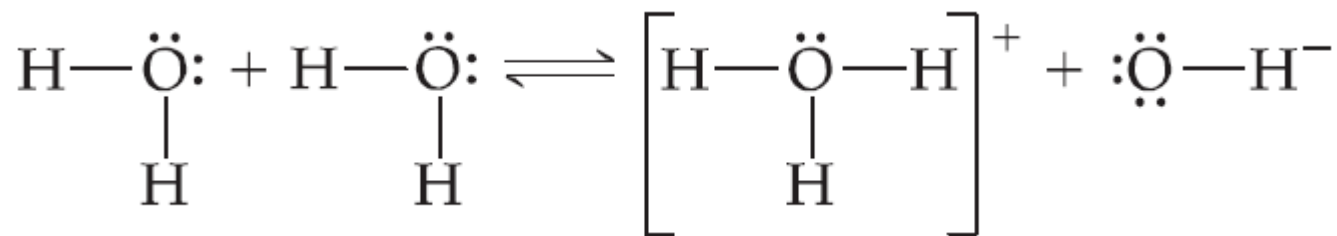
# **16.3**

## **The Autoionization of Water**

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# Autoionization of Water

Depending on the circumstances, water can act as either a Brønsted acid or a Brønsted base (water is **amphoteric**). In the presence of an acid, water acts as a proton acceptor; in the presence of a base, water acts as a proton donor. In fact, one water molecule can donate a proton to another water molecule.

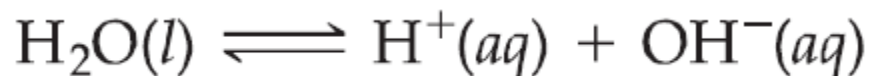
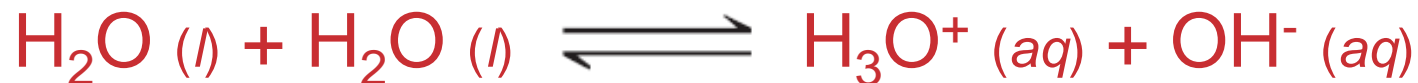


This is referred to as **autoionization of water**.

In pure water, a few molecules act as bases and a few act as acids.

At room temperature only about two out of every  $10^9$  molecules are ionized at any given instant. Thus, **pure water** consists almost entirely of  $\text{H}_2\text{O}$  molecules and is an **extremely poor conductor of electricity**. Nevertheless, the autoionization of water is very important.

# The Ion-Product Constant of Water



The equilibrium expression for this process is

$$K_c = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

This special equilibrium constant is referred to as **the ion-product constant** for water,  $K_w$ .

The term  $[\text{H}_2\text{O}]$  is excluded from the equilibrium-constant expression because we exclude the concentration of pure solids and liquids.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at 25 }^\circ\text{C)}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (\text{at } 25 \text{ }^\circ\text{C})$$

What makes this Equation particularly useful is that it is applicable to pure water and to any aqueous solution. Although the equilibrium between  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  as well as other ionic equilibria are affected somewhat by the presence of additional ions in solution.

A solution in which  $[\text{H}^+] = [\text{OH}^-]$  is said to be **neutral**.

In most solutions  $\text{H}^+$  and  $\text{OH}^-$  concentrations are not equal. As the concentration of one of these ions increases, the concentration of the other must decrease, so that the product of their concentrations equals  $1.0 \times 10^{-14}$ .

In **acidic** solutions  $[\text{H}^+]$  **exceeds**  $[\text{OH}^-]$ .

In **basic** solutions  $[\text{OH}^-]$  **exceeds**  $[\text{H}^+]$ .

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

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

### Solution

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

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

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

### Practice Exercise

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

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

*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  $1.8 \times 10^{-9}\ M$

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

### Solution

(a) Using Equation 16.14, 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

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

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# **16.4**

## **The pH Scale**

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# pH

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad \text{or} \quad \text{pH} = -\log [\text{H}^+]$$

- In pure water,

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14}$$

- Since in pure water  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ ,

$$[\text{H}_3\text{O}^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

- Therefore, in pure water,  

$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7.00$$
- An acid has a higher  $[\text{H}_3\text{O}^+]$  than pure water, so its pH is  $<7$ .
- A base has a lower  $[\text{H}_3\text{O}^+]$  than pure water, so its pH is  $>7$ .

Solution Type	$[\text{H}^+]$ (M)	$[\text{OH}^-]$ (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	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	$>7.00$

Because of the negative sign in Equation ( $\text{pH} = -\log[\text{H}^+]$ ), the pH decreases as  $[\text{H}^+]$  increases.

### Examples ...

$[\text{H}^+] = 1.0 \times 10^{-3}$  M calculate pH

$$\text{pH} = -\log(1.0 \times 10^{-3}) = -(-3.00) = 3$$

A sample of freshly pressed apple juice has a pH of 3.76, calculate  $[\text{H}^+]$

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

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

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

	$[H^+]$ (M)	pH	pOH	$[OH^-]$ (M)
	$1 (1 \times 10^{-0})$	<b>0.0</b>	<b>14.0</b>	$1 \times 10^{-14}$
Gastric juice	$1 \times 10^{-1}$	<b>1.0</b>	<b>13.0</b>	$1 \times 10^{-13}$
Lemon juice	$1 \times 10^{-2}$	<b>2.0</b>	<b>12.0</b>	$1 \times 10^{-12}$
Cola, vinegar	$1 \times 10^{-3}$	<b>3.0</b>	<b>11.0</b>	$1 \times 10^{-11}$
Wine	$1 \times 10^{-4}$	<b>4.0</b>	<b>10.0</b>	$1 \times 10^{-10}$
Tomatoes	$1 \times 10^{-5}$	<b>5.0</b>	<b>9.0</b>	$1 \times 10^{-9}$
Banana	$1 \times 10^{-6}$	<b>6.0</b>	<b>8.0</b>	$1 \times 10^{-8}$
Black coffee	$1 \times 10^{-7}$	<b>7.0</b>	<b>7.0</b>	$1 \times 10^{-7}$
Rain	$1 \times 10^{-8}$	<b>8.0</b>	<b>6.0</b>	$1 \times 10^{-6}$
Saliva	$1 \times 10^{-9}$	<b>9.0</b>	<b>5.0</b>	$1 \times 10^{-5}$
Milk	$1 \times 10^{-10}$	<b>10.0</b>	<b>4.0</b>	$1 \times 10^{-4}$
Human blood, tears	$1 \times 10^{-11}$	<b>11.0</b>	<b>3.0</b>	$1 \times 10^{-3}$
Egg white, seawater	$1 \times 10^{-12}$	<b>12.0</b>	<b>2.0</b>	$1 \times 10^{-2}$
Baking soda	$1 \times 10^{-13}$	<b>13.0</b>	<b>1.0</b>	$1 \times 10^{-1}$
Borax	$1 \times 10^{-14}$	<b>14.0</b>	<b>0.0</b>	$1 (1 \times 10^{-0})$
Milk of magnesia				
Lime water				
Household ammonia				
Household bleach				
NaOH, 0.1 M				

These are the pH values for several common substances at 25 °C.

The pH of a solution can be estimated using the benchmark concentrations of  $H^+$  and  $OH^-$  corresponding to whole number pH values.

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

Calculate the pH values for;

(a) a solution with  $[OH^-]$  is  $0.010\ M$ , (b) a solution with  $[OH^-]$  is  $1.8 \times 10^{-9}\ M$ .

### Solution

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

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

Because  $1.0 \times 10^{-12}$  has two significant figures, the pH has two decimal places, **12.00**.

(b)  $[H^+] = 5.6 \times 10^{-6}\ M$ . Before performing the calculation, it is helpful to estimate the pH. To do so, we note that  $[H^+]$  lies between  $1 \times 10^{-6}$  and  $1 \times 10^{-5}$

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

Thus, we expect the pH to lie between 6.0 and 5.0.

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

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

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

### Solution

From Equation 16.17, we have

Thus,

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:

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

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

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

**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.

# pOH and 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

- $\text{pOH} = -\log [\text{OH}^-]$

- $\text{p}K_w = -\log K_w$

$$\text{px} = -\log x$$

Larger the x, smaller the px

Because

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

we know that

$$-\log [\text{H}_3\text{O}^+] + -\log [\text{OH}^-] = -\log K_w = 14.00$$

or, in other words,

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

# Measuring pH

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

The device is a **millivoltmeter**, and the electrodes immersed in the solution being tested produce a voltage that depends on the pH of the solution.



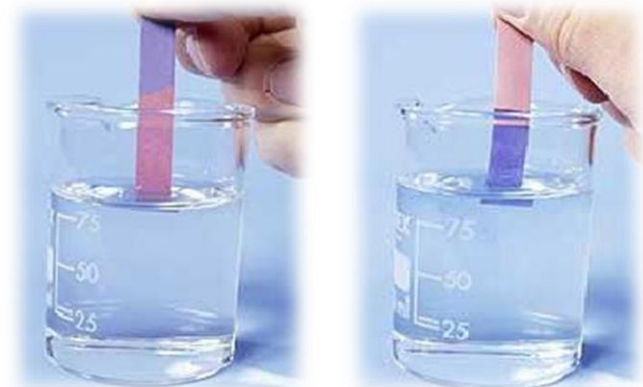
A voltage (in millivolts), which varies with the pH, is generated when the electrodes are placed in a solution. This voltage is read by the meter, which is calibrated to give pH.

For less accurate measurements, one can use

– **Indicators:** special chemicals that change color if there is a change in the pH (caused by adding an acid or alkali). Indicators change color at different pH values.

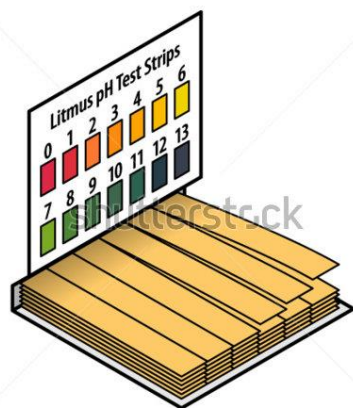
– **Litmus paper**

- “Red” paper turns blue above  $\sim\text{pH} = 8$
- “Blue” paper turns red below  $\sim\text{pH} = 5$

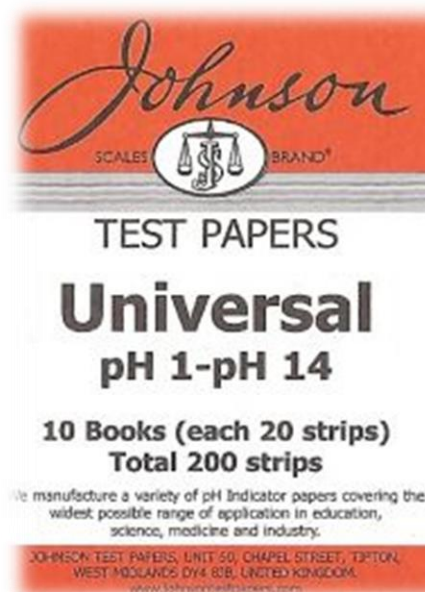


– **Universal indicator papers**

Papers impregnated with several indicators.



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METHOD FOR GENERAL USE  
A strip of the test paper should be dipped into the test solution for approximately one second and then removed. Compare the colour produced on the test paper with the colour chart by holding it against the nearest matching colour within 5 seconds of removal. The colour produced will indicate the pH of the solution. For turbid liquid/suspensions place a drop of test liquid onto a strip of test paper. Use the spot on the reverse side of the test paper to compare with the colour chart.



**IMPORTANT:** Do not store indicator papers where they are liable to be exposed to dust or other foreign matter.



	pH range for color change													
	0	2	4	6	8	10	12	14						
Methyl violet	Yellow		Violet											
Thymol blue		Red		Yellow		Yellow		Blue						
Methyl orange			Red		Yellow									
Methyl red				Red		Yellow								
Bromthymol blue					Yellow		Blue							
Phenolphthalein						Colorless		Pink						
Alizarin yellow R								Yellow		Red				

The pH ranges for the color changes of some common acid-base indicators.

Most indicators have a useful range of about 2 pH units.

Methyl orange changes color over the pH interval from 3.1 to 4.4. Below pH 3.1 it is in the acid form (red). In the interval between 3.1 and 4.4, it is gradually converted to its basic form, which has a yellow color. By pH 4.4 the conversion is complete, and the solution is yellow.

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# **16.5**

## **Strong Acids and Bases**

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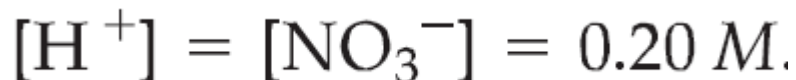
- The seven most common **strong acids** are HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>3</sub>, and HClO<sub>4</sub> (monoprotic) and H<sub>2</sub>SO<sub>4</sub> (diprotic).
- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.
- For the monoprotic strong acids,



Strong acids are strong electrolytes, existing in aqueous solution entirely as ions.

For example,

0.20 M solution of HNO<sub>3</sub>(aq)



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

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

### Solution

The pH of the solution is given by

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

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

- **Strong bases** are the soluble hydroxides, which are the alkali metal (group 1A) hydroxides ( $\text{Na}^{+1}$  and  $\text{K}^{+1}$ ) and heavier alkaline earth metal (group 2A) hydroxides ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ ).

- Again, these substances dissociate completely in aqueous solution.

hydrogen 1 H 1.0079		
lithium 3 Li 6.941	beryllium 4 Be 9.0122	
sodium 11 Na 22.990	magnesium 12 Mg 24.305	
potassium 19 K 39.098	calcium 20 Ca 40.078	
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	
caesium 55 Cs 132.91	barium 56 Ba 137.33	57- *
francium 87 Fr [223]	radium 88 Ra [226]	89-1 *

Strong bases are strong electrolytes, existing in aqueous solution entirely as ions.

For example,

0.30 M NaOH consists of

0.30 M  $\text{Na}^{+}(aq)$  and 0.30 M  $\text{OH}^{-}(aq)$

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

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

### Solution

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

*Method 1:*

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

*Method 2:*

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

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

*Method 1:*

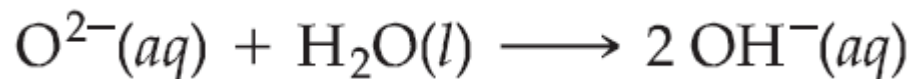
$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.0022} = 4.55 \times 10^{-12} \text{ M} \quad \text{pH} = -\log(4.55 \times 10^{-12}) = 11.34$$

*Method 2:*

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

Although all the hydroxides of the alkali metals (group 1A) are strong electrolytes, LiOH, RbOH, and CsOH are not commonly encountered in the laboratory. The hydroxides of the heavier alkaline earth metals  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ , and  $\text{Ba}(\text{OH})_2$ , are also strong electrolytes. They have limited solubilities, however, so they are used only when high solubility is not critical.

Another strong bases include the **oxide ion**. **Ionic metal oxides**, especially  $\text{Na}_2\text{O}$  and  $\text{CaO}$ , are often used in industry when a strong base is needed. The  $\text{O}^{2-}$  reacts with water to form  $\text{OH}^-$ , leaving virtually no  $\text{O}^{2-}$  remaining in the solution:



Thus, a solution formed by dissolving 0.010 mol of  $\text{Na}_2\text{O}(\text{s})$  in enough water to form 1.0 L of solution will have  $[\text{OH}^-] = 0.020 \text{ M}$  and a pH of 12.30.

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# **16.6**

## **Weak Acids**

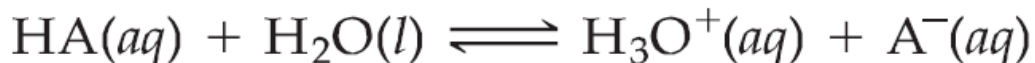
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# Dissociation Constants

Most acidic substances are weak acids and are therefore only partially ionized in aqueous solution. We can use the equilibrium constant for the ionization reaction to express the extent to which a weak acid ionizes.

- For a generalized acid dissociation,



or

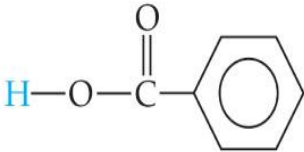
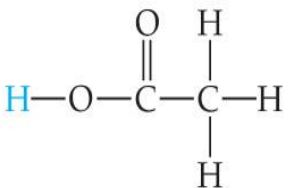
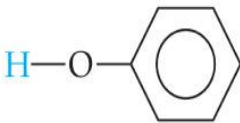


Either of the following ways, depending on whether the hydrated proton is represented as  $\text{H}_3\text{O}^+(aq)$  or  $\text{H}^+(aq)$ :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

This equilibrium constant  $K_a$  is called the **acid-dissociation constant**. Because  $\text{H}_2\text{O}$  is the solvent, it is omitted from the equilibrium-constant expression.

The magnitude of  $K_a$  indicates the tendency of the acid to ionize in water, **the larger the value of  $K_a$ , the stronger the acid**. Hydrofluoric acid (HF), for example, is the strongest acid listed in Table, and phenol ( $\text{HOC}_6\text{H}_5$ ) is the weakest.

Acid	Structural Formula*	Conjugate Base	Equilibrium Reaction	$K_a$
Hydrofluoric (HF)	$\text{H}-\text{F}$	$\text{F}^-$	$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$	$6.8 \times 10^{-4}$
Nitrous ( $\text{HNO}_2$ )	$\text{H}-\text{O}-\text{N}=\text{O}$	$\text{NO}_2^-$	$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)$	$4.5 \times 10^{-4}$
Benzoic ( $\text{C}_6\text{H}_5\text{COOH}$ )		$\text{C}_6\text{H}_5\text{COO}^-$	$\text{C}_6\text{H}_5\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_6\text{H}_5\text{COO}^-(aq)$	$6.3 \times 10^{-5}$
Acetic ( $\text{CH}_3\text{COOH}$ )		$\text{CH}_3\text{COO}^-$	$\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$	$1.8 \times 10^{-5}$
Hypochlorous ( $\text{HClO}$ )	$\text{H}-\text{O}-\text{Cl}$	$\text{ClO}^-$	$\text{HClO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}^-(aq)$	$3.0 \times 10^{-8}$
Hydrocyanic ( $\text{HCN}$ )	$\text{H}-\text{C}\equiv\text{N}$	$\text{CN}^-$	$\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)$	$4.9 \times 10^{-10}$
Phenol ( $\text{HOC}_6\text{H}_5$ )		$\text{C}_6\text{H}_5\text{O}^-$	$\text{HC}_6\text{H}_5\text{O}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_6\text{H}_5\text{O}^-(aq)$	$1.3 \times 10^{-10}$

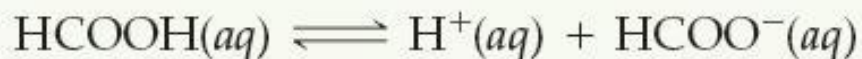
\* The proton that ionizes is shown in blue.

In almost all cases the hydrogen atoms bonded to carbon do not ionize in water; instead, the acidic behavior of these compounds is due to the hydrogen atoms attached to oxygen atoms.

## 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 °C was found to be 2.38. Calculate  $K_a$  for formic acid at this temperature.

### Solution



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

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

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

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

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

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

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

# Percent Ionization

The magnitude of  $K_a$  indicates the strength of a weak acid. Another measure of acid strength is percent ionization, which is defined as

$$\text{Percent ionization} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%$$

The stronger the acid, the greater is the percent ionization.

For any acid, the concentration of acid that undergoes ionization equals the concentration of  $\text{H}^+(\text{aq})$  that forms, assuming that the autoionization of water is negligible.

$$\text{Percent ionization} = \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HA}]_{\text{initial}}} \times 100\%$$

For example, a 0.035 M solution of  $\text{HNO}_2$  contains  $3.7 \times 10^{-3}$  M  $\text{H}^+(\text{aq})$ . Thus, the percent ionization is

$$\text{Percent ionization} = \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HNO}_2]_{\text{initial}}} \times 100\% = \frac{3.7 \times 10^{-3} \text{ M}}{0.035 \text{ M}} \times 100\% = 11\%$$

## Sample Exercise 16.11 Calculating Percent Ionization

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

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

# Calculating pH from $K_a$

Calculate the pH of a 0.30 M solution of acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , at 25 °C.



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

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$



Initial	0.30 M	0	0
Change	$-x$ M	$+x$ M	$+x$ M
Equilibrium	$(0.30 - x)$ M	$x$ M	$x$ M

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5}$$

$$0.30 - x \simeq 0.30$$

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

$$x^2 = (0.30)(1.8 \times 10^{-5}) = 5.4 \times 10^{-6}$$

$$x = \sqrt{5.4 \times 10^{-6}} = 2.3 \times 10^{-3}$$

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

$$\text{pH} = -\log(2.3 \times 10^{-3}) = 2.64$$

Percent ionization of  $\text{CH}_3\text{COOH} =$

$$\frac{0.0023 \text{ M}}{0.30 \text{ M}} \times 100\% = 0.77\%$$

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

Calculate the pH of a 0.20 M solution of HCN ( $K_a = 4.9 \times 10^{-10}$ ).

### Solution



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

	HCN(aq)	$\rightleftharpoons$	H <sup>+</sup> (aq)	+	CN <sup>-</sup> (aq)
Initial	0.20 M		0		0
Change	-x M		+x M		+x M
Equilibrium	(0.20 - x) M		x M		x M

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

$$0.20 - x \simeq 0.20$$

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

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

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

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



The properties of the acid solution that relate directly to the concentration of  $\text{H}^+(\text{aq})$ .

The Figures compare the behavior of 1 M  $\text{CH}_3\text{COOH}$  and 1 M  $\text{HCl}$ . The 1 M  $\text{CH}_3\text{COOH}$  contains only 0.004 M  $\text{H}^+(\text{aq})$ , whereas the 1 M  $\text{HCl}$  solution contains 1 M  $\text{H}^+(\text{aq})$ . As a result, the rate of reaction is much faster for the solution of  $\text{HCl}$ .

(a) the flask on the left contains 1 M  $\text{CH}_3\text{COOH}$ , the one on the right contains 1 M  $\text{HCl}$  with the same amount of magnesium metal.

(b) when the  $\text{Mg}$  is dropped into the acid,  $\text{H}_2$  gas is formed. The rate of  $\text{H}_2$  formation is higher for  $\text{HCl}$  on the right. Eventually, the same amount of  $\text{H}_2$  forms in both cases.



(a)



(b)

## 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

(a)

Initial	0.10 M	0	0
Change	-x M	+x M	+x M
Equilibrium	(0.10 - x) M	x M	x M

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{0.10 - x} = 6.8 \times 10^{-4} \quad x = 8.2 \times 10^{-3} \text{ M}$$

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

$$= 6.8 \times 10^{-5} - (6.8 \times 10^{-4})x$$

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

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

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

$$= \frac{-6.8 \times 10^{-4} \pm 1.6 \times 10^{-2}}{2}$$

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

$$\text{Percent ionization of HF} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%$$

$$= \frac{7.9 \times 10^{-3} \text{ M}}{0.10 \text{ M}} \times 100\% = 7.9\%$$

(b)

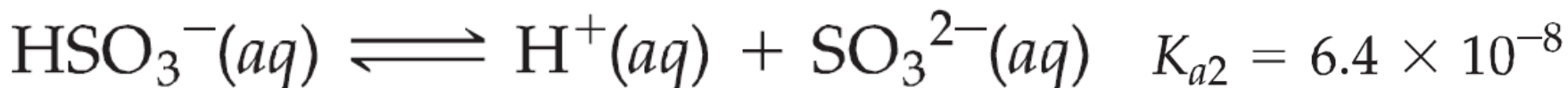
$$\frac{x^2}{0.010 - x} = 6.8 \times 10^{-4}$$

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

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

# Polyprotic Acids

Polyprotic acids have more than one ionizable H atom



The acid dissociation constants for these equilibria are labeled  $K_{a1}$  and  $K_{a2}$ .

In the preceding example  $K_{a2}$  is much smaller than  $K_{a1}$ .

**It is always easier to remove the first proton from a polyprotic acid than to remove the second.**

Similarly, for an acid with three ionizable protons, it is easier to remove the second proton than the third. Thus, the  $K_a$  values become successively smaller as successive protons are removed.

**TABLE 16.3 ■ Acid-Dissociation Constants of Some Common Polyprotic Acids**

Name	Formula	$K_{a1}$	$K_{a2}$	$K_{a3}$
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	$8.0 \times 10^{-5}$	$1.6 \times 10^{-12}$	
Carbonic	$\text{H}_2\text{CO}_3$	$4.3 \times 10^{-7}$	$5.6 \times 10^{-11}$	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	$7.4 \times 10^{-4}$	$1.7 \times 10^{-5}$	$4.0 \times 10^{-7}$
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	$5.9 \times 10^{-2}$	$6.4 \times 10^{-5}$	
Phosphoric	$\text{H}_3\text{PO}_4$	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.2 \times 10^{-13}$
Sulfurous	$\text{H}_2\text{SO}_3$	$1.7 \times 10^{-2}$	$6.4 \times 10^{-8}$	
Sulfuric	$\text{H}_2\text{SO}_4$	Large	$1.2 \times 10^{-2}$	
Tartaric	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	$1.0 \times 10^{-3}$	$4.6 \times 10^{-5}$	

Sulfuric acid is strong acid with respect to the removal of the first proton. Thus, the reaction for the first ionization step lies completely to the right:



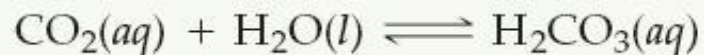
$\text{HSO}_4^-$ , on the other hand, is a weak acid for which  $K_{a2} = 1.2 \times 10^{-2}$ .

Because  $K_{a1}$  is so much larger than subsequent dissociation constants for these polyprotic acids, most of the  $\text{H}^+(aq)$  in the solution comes from the first ionization reaction. As long as successive  $K_a$  values differ by a factor of  $10^3$ .

If the difference between the  $K_{a1}$  for the first dissociation and subsequent  $K_{a2}$  values is  $10^3$  or more, the pH generally depends *only* on the first dissociation.

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

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



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

### Solution



Initial	0.0037 M	0	0
Change	$-x$ M	$+x$ M	$+x$ M
Equilibrium	$(0.0037 - x)$ M	$x$ M	$x$ M

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

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

$$0.0037 - x \approx 0.0037$$

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

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

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

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



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

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

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

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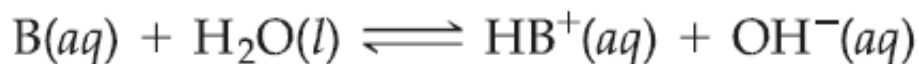
# **16.7**

## **Weak Bases**

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Many substances behave as weak bases in water. Weak bases react with water, abstracting protons from H<sub>2</sub>O, thereby forming the conjugate acid of the base and OH<sup>-</sup> ions.

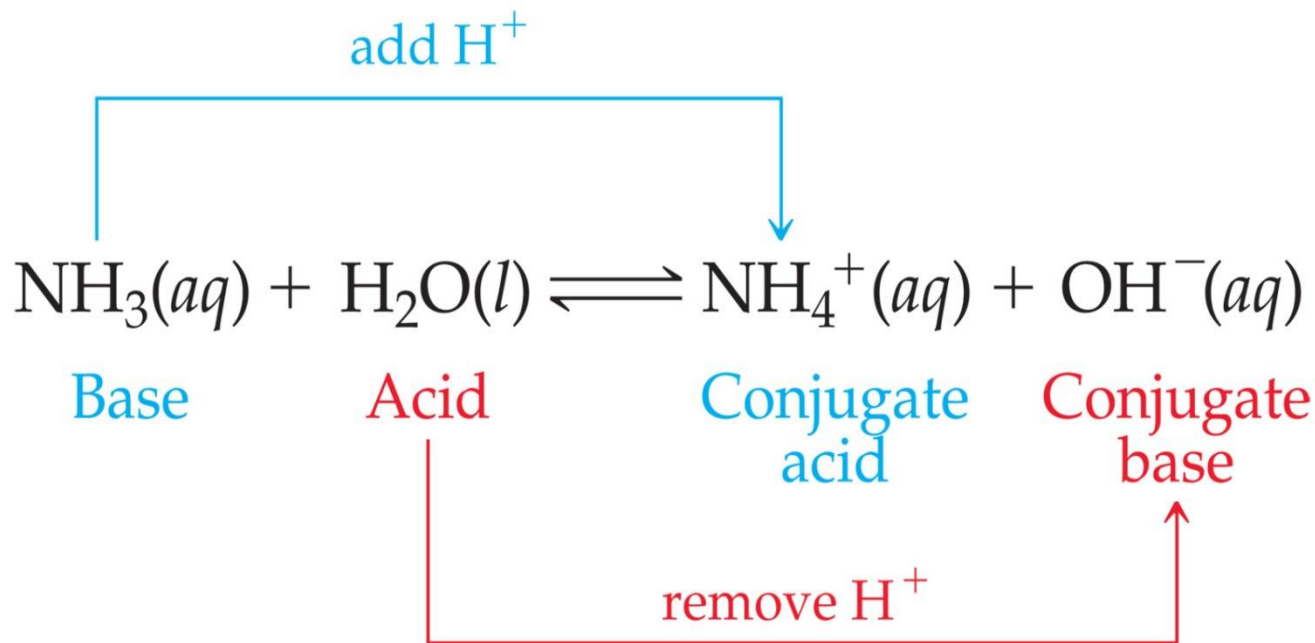
Bases react with water to produce hydroxide ion.



The equilibrium constant expression for this reaction can be written as

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The constant  $K_b$  is called the **base-dissociation constant**. The constant  $K_b$  always refers to the equilibrium in which a base reacts with H<sub>2</sub>O to form the corresponding conjugate acid and OH<sup>-</sup>.




The equilibrium constant expression for this reaction is

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



Lists the names, formulas, Lewis structures, equilibrium reactions and values of  $K_b$  for several weak bases in water.

Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	$K_b$
Ammonia (NH <sub>3</sub> )	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\   \\ \text{H} \end{array}$	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub> + H <sub>2</sub> O $\rightleftharpoons$ NH <sub>4</sub> <sup>+</sup> + OH <sup>-</sup>	$1.8 \times 10^{-5}$
Pyridine (C <sub>5</sub> H <sub>5</sub> N)		C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup>	C <sub>5</sub> H <sub>5</sub> N + H <sub>2</sub> O $\rightleftharpoons$ C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup> + OH <sup>-</sup>	$1.7 \times 10^{-9}$
Hydroxylamine (H <sub>2</sub> NOH)	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\ddot{\text{O}}\text{H} \\   \\ \text{H} \end{array}$	H <sub>3</sub> NOH <sup>+</sup>	H <sub>2</sub> NOH + H <sub>2</sub> O $\rightleftharpoons$ H <sub>3</sub> NOH <sup>+</sup> + OH <sup>-</sup>	$1.1 \times 10^{-8}$
Methylamine (NH <sub>2</sub> CH <sub>3</sub> )	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{CH}_3 \\   \\ \text{H} \end{array}$	NH <sub>3</sub> CH <sub>3</sub> <sup>+</sup>	NH <sub>2</sub> CH <sub>3</sub> + H <sub>2</sub> O $\rightleftharpoons$ NH <sub>3</sub> CH <sub>3</sub> <sup>+</sup> + OH <sup>-</sup>	$4.4 \times 10^{-4}$
Hydrosulfide ion (HS <sup>-</sup> )	$\left[ \text{H}-\ddot{\text{S}} \right]^{-}$	H <sub>2</sub> S	HS <sup>-</sup> + H <sub>2</sub> O $\rightleftharpoons$ H <sub>2</sub> S + OH <sup>-</sup>	$1.8 \times 10^{-7}$
Carbonate ion (CO <sub>3</sub> <sup>2-</sup> )	$\left[ \begin{array}{c} \ddot{\text{O}} \\   \\ \text{C} \\ / \quad \backslash \\ \ddot{\text{O}} \quad \ddot{\text{O}} \end{array} \right]^{2-}$	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup> + H <sub>2</sub> O $\rightleftharpoons$ HCO <sub>3</sub> <sup>-</sup> + OH <sup>-</sup>	$1.8 \times 10^{-4}$
Hypochlorite ion (ClO <sup>-</sup> )	$\left[ \ddot{\text{Cl}}-\ddot{\text{O}} \right]^{-}$	HClO	ClO <sup>-</sup> + H <sub>2</sub> O $\rightleftharpoons$ HClO + OH <sup>-</sup>	$3.3 \times 10^{-7}$

These bases contain one or more lone pairs of electrons because a lone pair is necessary to form the bond with H<sup>+</sup>. Notice that in the neutral molecules in the Table, the lone pairs are on nitrogen atoms. The other bases listed are anions derived from weak acids.

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

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

### Solution



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



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

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

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

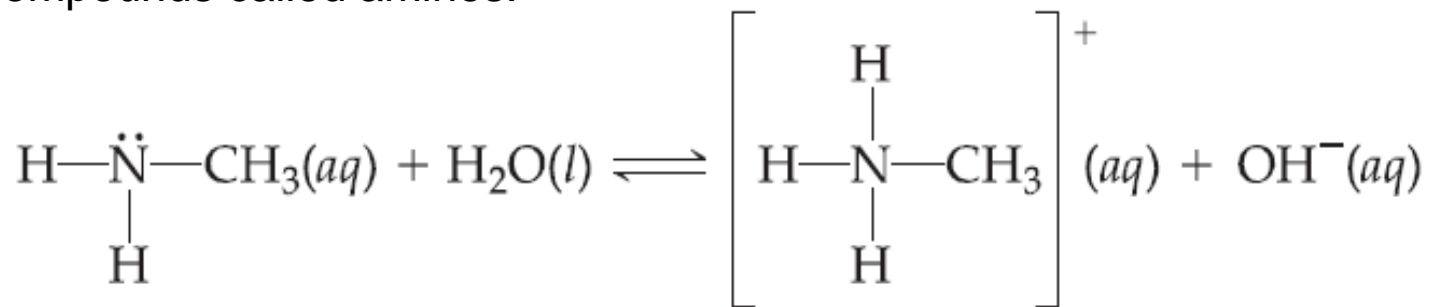
$$x^2 = (0.15)(1.8 \times 10^{-5}) = 2.7 \times 10^{-6}$$

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

# Types of Weak Bases

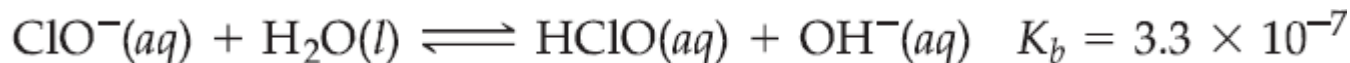
Weak bases fall into two categories:

-The first category contains **neutral substances that have an atom with a nonbonding pair of electrons** that can serve as a proton acceptor. Most of these bases contain a nitrogen atom. These substances include ammonia and a related class of compounds called amines.



The chemical formula for the conjugate acid of methylamine is usually written  $\text{CH}_3\text{NH}_3^+$ .

-The second general category of weak bases consists of the **anions of weak acids**. For example,  $\text{NaClO}$  dissociates to give  $\text{Na}^+$  and  $\text{ClO}^-$  ions.  $\text{Na}^+$  ion is a spectator ion.  $\text{ClO}^-$  ion is the conjugate base of a weak acid, hypochlorous acid  $\text{HClO}$ . Consequently, the  $\text{ClO}^-$  ion acts as a weak base in water:



## 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. Calculate the number of moles of NaClO that were added to the water. ( $K_b = 3.3 \times 10^{-7}$ ).

### Solution

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.50 = 3.50$$

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



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

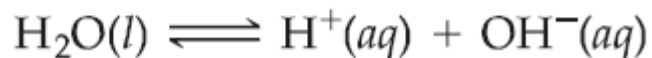
$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{(3.2 \times 10^{-4})^2}{x - 3.2 \times 10^{-4}} = 3.3 \times 10^{-7}$$

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

# 16.8

## Relationship Between $K_a$ and $K_b$

To see if we can find a corresponding quantitative relationship, let's consider the  $\text{NH}_4^+$  and  $\text{NH}_3$  conjugate acid-base pair. Each of these species reacts with water:



$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

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

$$\begin{aligned} K_a \times K_b &= \left( \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \right) \left( \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \right) \\ &= [\text{H}^+][\text{OH}^-] = K_w \end{aligned}$$

$K_a$  and  $K_b$  are related in this way:

$$\mathbf{K_a \times K_b = K_w}$$

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

This relationship is so important that it should receive special attention: The product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base equals the ion-product constant for water.

$$K_a \times K_b = K_w$$

As the strength of an acid increases (larger  $K_a$ ), the strength of its conjugate base must decrease (smaller  $K_b$ ) so that the product  $K_a \times K_b$  equals  $1.0 \times 10^{-14}$  at 25 °C. Remember, this important relationship applies only to **conjugate acid-base pairs**.

Last Equation can be written in terms of  $pK_a$  and  $pK_b$  by taking the negative log of both sides:

$$pK_a + pK_b = pK_w = 14.00 \quad \text{at } 25 \text{ } ^\circ\text{C}$$

## Some Conjugate Acid–Base Pairs

Acid	$K_a$	Base	$K_b$
HNO <sub>3</sub>	(Strong acid)	NO <sub>3</sub> <sup>-</sup>	(Negligible basicity)
HF	$6.8 \times 10^{-4}$	F <sup>-</sup>	$1.5 \times 10^{-11}$
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	$1.8 \times 10^{-5}$	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	$5.6 \times 10^{-10}$
H <sub>2</sub> CO <sub>3</sub>	$4.3 \times 10^{-7}$	HCO <sub>3</sub> <sup>-</sup>	$2.3 \times 10^{-8}$
NH <sub>4</sub> <sup>+</sup>	$5.6 \times 10^{-10}$	NH <sub>3</sub>	$1.8 \times 10^{-5}$
HCO <sub>3</sub> <sup>-</sup>	$5.6 \times 10^{-11}$	CO <sub>3</sub> <sup>2-</sup>	$1.8 \times 10^{-4}$
OH <sup>-</sup>	(Negligible acidity)	O <sup>2-</sup>	(Strong base)



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

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

- $K_a$  for the weak acid HF,  $K_a = 6.8 \times 10^{-4}$ .
- $K_b$  for weak base  $NH_3$ ,  $K_b = 1.8 \times 10^{-5}$ .

### Solution

(a)  $K_a$  for HF =  $6.8 \times 10^{-4}$ . We can 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  $NH_3 = 1.8 \times 10^{-5}$ . we can calculate  $K_a$  for the conjugate acid,  $NH_4^+$ :

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

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# **16.9**

## **Acid-Base Properties of Salt Solutions**

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## Ions can also exhibit acidic or basic properties.

**Salt** solutions can be acidic or basic.

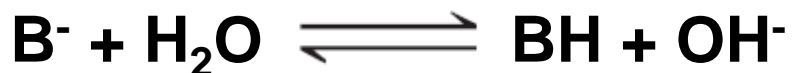
Because **nearly all salts are strong electrolytes**, we can assume that when salts dissolve in water, they are completely dissociated.

Consequently, the acid-base properties of salt solutions are due to the behavior of their constituent cations and anions.

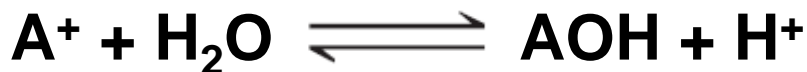
Many ions are able to react with water to generate  $\text{H}^+_{(\text{aq})}$  or  $\text{OH}^-_{(\text{aq})}$ . This type of reaction is often called **hydrolysis**. The pH of an aqueous salt solution can be predicted qualitatively by considering the ions of which the salt is composed.

# Effect of Cation and Anion in Solution

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. **Cations** of the **strong bases** will not affect the pH.
4. A **cation** that is the conjugate acid of a **weak base** will decrease the pH.



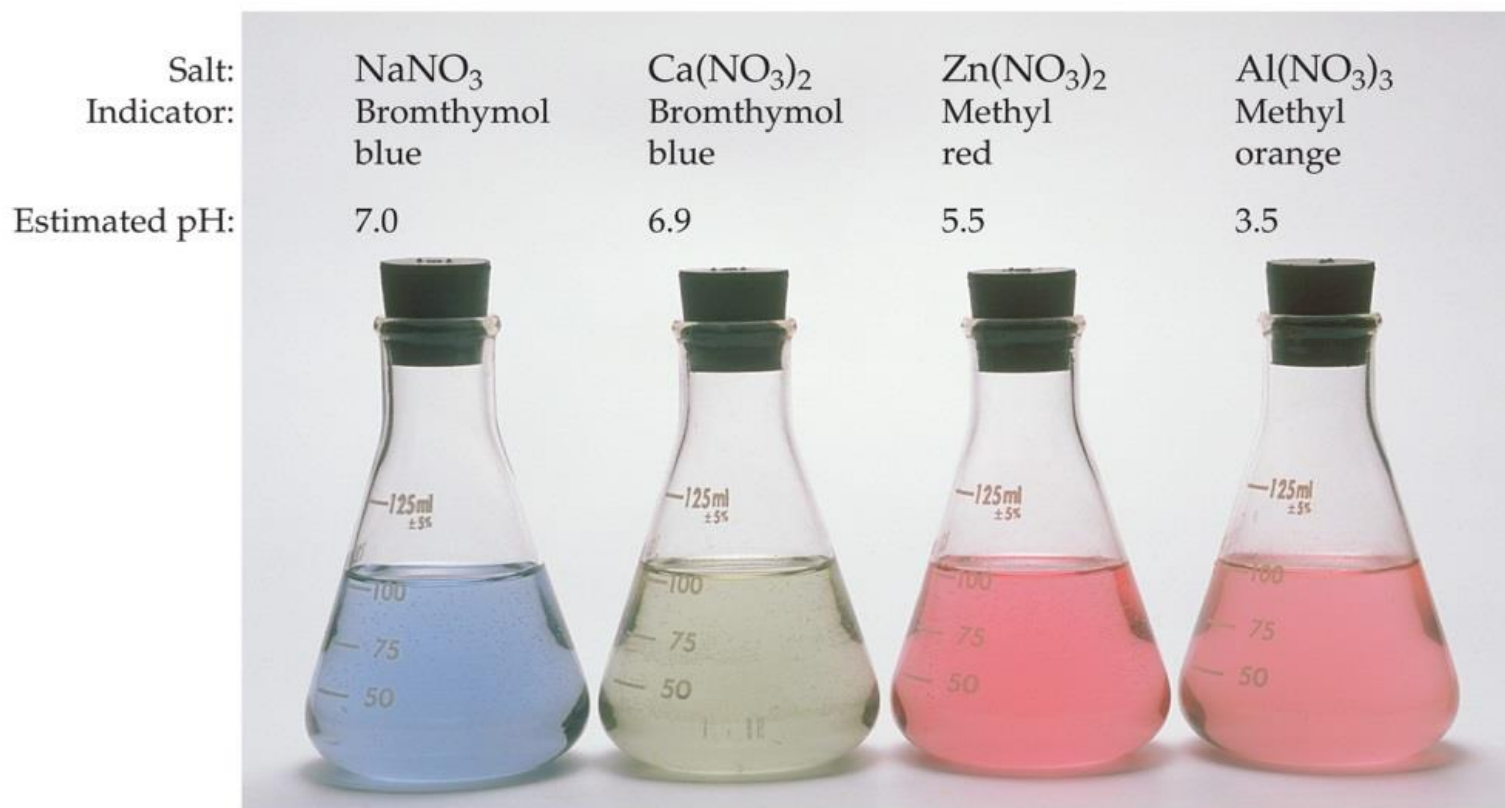
4. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the  $K_a$  and  $K_b$  values:
  - If  $K_a > K_b$ , the ion will cause the solution to be acidic.
  - If  $K_b > K_a$ , the solution will be basic.



Salt solutions can be neutral, acidic, or basic. These three solutions contain the acid-base indicator bromthymol blue.

- (a) NaCl solution is neutral (pH = 7.0)**
- (b)  $\text{NH}_4\text{Cl}$  solution is acidic (pH = 3.5)**
- (c) NaClO solution is basic (pH = 9.5)**

This Figure demonstrates the influence of several salts on pH.



## We can summarize the chapter as follows:

- For **strong acid** and **bases**, they will be **completely ionize** to 100%.
- For **weak acids** and **bases** we can use the dissociation constants,  $k_a$  and  $k_b$  to find the amount that has been dissociated.
- For salts when they dissolve in water ( $H^+$ )( $OH^-$ ), they can produce acidic or basic solutions based on the type the reaction of the anion and the cations of the salt with ( $H^+$ ) or ( $OH^-$ ) of the water:
  - If the anion in the salt is a conjugate base of strong acid such as HCl, the acid will not form in this direction and consequently the ( $H^+$ ) will not form and no change in pH will result.
  - If the anion salt is a conjugate base of weak acids such as acetic acid, the acid will form and the hydroxide ions will form as well ( $OH^-$ ) giving basic solution.
  - For the cation in the salt if it is a cation of the 1<sup>st</sup> or 2<sup>nd</sup> A groups, they will not affect the pH but if they are transition metals, they will abstract the ( $OH^-$ ) ions from water and result in formation of ( $H^+$ ) ions leading to acidic solution. Such effect will depend on the dissociation constants.

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

Determine whether aqueous solutions of each of the following salts will be acidic, basic, or neutral:

(a)  $\text{Ba}(\text{CH}_3\text{COO})_2$ , (b)  $\text{NH}_4\text{Cl}$ , (c)  $\text{CH}_3\text{NH}_3\text{Br}$ , (d)  $\text{KNO}_3$ , (e)  $\text{Al}(\text{ClO}_4)_3$ .

### Solution

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

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

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

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

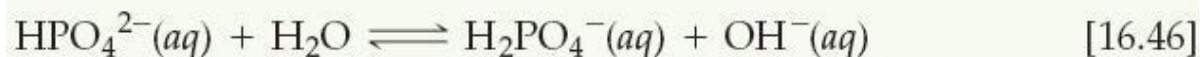
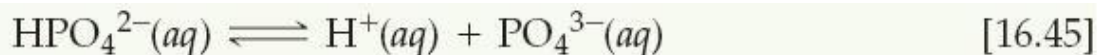
(e) This solution contains  $\text{Al}^{3+}$  and  $\text{ClO}_4^-$  ions. Cations, such as  $\text{Al}^{3+}$ , that are not in groups 1A or 2A are acidic. The  $\text{ClO}_4^-$  ion is the conjugate base of a strong acid ( $\text{HClO}_4$ ) and therefore does not affect pH. Thus, the solution of  $\text{Al}(\text{ClO}_4)_3$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



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

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

### Solution



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

The value of  $K_a$  for Equation 16.45, is  $4.2 \times 10^{-13}$ .

We must calculate the value of  $K_b$  for Equation 16.46 from the value of  $K_a$  for its conjugate acid,  $\text{H}_2\text{PO}_4^-$ .

$$K_a \times K_b = K_w$$

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

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

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



**Q & A**



# A Brønsted–Lowry acid is:

- a. a proton donor.
- b. a proton acceptor.
- c. an electron-pair donor.
- d. an electron-pair acceptor.

# A Lewis acid is:

- a. a proton donor.
- b. a proton acceptor.
- c. an electron-pair donor.
- d. an electron-pair acceptor.

What is the conjugate base of  $\text{HPO}_4^{2-}$  ?

- a.  $\text{H}_3\text{PO}_4$
- b.  $\text{H}_2\text{PO}_4^{1-}$
- c.  $\text{PO}_4^{3-}$
- d.  $\text{HPO}_3^{2-}$

What is the conjugate acid of  $\text{SO}_4^{2-}$  ?

- a.  $\text{H}_2\text{SO}_4$
- b.  $\text{HSO}_4^{1-}$
- c.  $\text{SO}_3^{2-}$
- d.  $\text{H}_3\text{SO}_4^+$

The stronger the acid, the (X) its conjugate base. Acids and bases generally react to form their (Y) conjugates.

- a. X = stronger, Y = stronger
- b. X = stronger, Y = weaker
- c. X = weaker, Y = stronger
- d. X = weaker, Y = weaker

What is the pH of a 0.0200 *M* aqueous solution of HBr ?

a. 1.00

b. 1.70

c. 2.30

d. 12.30



What is the pH of a 0.0400 *M* aqueous solution of KOH ?

a. 12.60

b. 10.30

c. 4.00

d. 1.40

The  $K_a$  of HF is  $6.8 \times 10^{-4}$ . What is the pH of a 0.0200 M aqueous solution of HF ?

a. 1.70

b. 2.43

c. 3.17

d. 12.30

The  $K_a$  of HF is  $6.8 \times 10^{-4}$ . What is the pH of a 0.0400 M aqueous solution of KF ?

- a. 2.28
- b. 2.43
- c. 6.12
- d. 7.88

Which choice correctly lists the acids in decreasing order of acid strength ?

- a.  $\text{HClO}_2 > \text{HClO} > \text{HBrO} > \text{HIO}$
- b.  $\text{HClO} > \text{HBrO} > \text{HIO} > \text{HClO}_2$
- c.  $\text{HIO} > \text{HBrO} > \text{HClO} > \text{HClO}_2$
- d.  $\text{HClO}_2 > \text{HIO} > \text{HBrO} > \text{HClO}$

# Which base is the weakest ?

- $F^-$
- $NH_3$
- $OH^-$
- $SO_4^{2-}$
- $C_2H_3O_2^-$

# Which acid is the strongest ?

- $\text{H}_2\text{O}$
- $\text{H}_3\text{O}^+$
- $\text{HF}$
- $\text{HC}_2\text{H}_3\text{O}_2$
- $\text{NH}_4^+$

# Which base is the strongest ?

- $\text{NO}_3^-$
- $\text{C}_2\text{H}_3\text{O}_2^-$
- $\text{HCO}_3^-$
- $\text{CO}_3^{2-}$
- $\text{NH}_3$

Acid	Ka
$\text{HNO}_3$	(Strong acid)
HF	$6.8 * 10^{-4}$
$\text{HC}_2\text{H}_3\text{O}_2$	$1.8 * 10^{-5}$
$\text{H}_2\text{CO}_3$	$4.3 * 10^{-7}$
$\text{NH}_4^+$	$5.6 * 10^{-10}$
$\text{HCO}_3^-$	$5.6 * 10^{-11}$
$\text{OH}^-$	(Negligible acidity)

If the  $\text{pH} = 2$  for an  $\text{HNO}_3$  solution, what is the concentration of  $\text{HNO}_3$ ?

- 0.10
- 0.20
- 0.010
- 0.020
- 0.0010



If the  $\text{pH} = 10$  for a  $\text{Ca}(\text{OH})_2$  solution, what is the concentration of  $\text{Ca}(\text{OH})_2$ ?

- $1.0 \times 10^{-10}$
- $5.0 \times 10^{-11}$
- $5.0 \times 10^{-3}$
- $1.0 \times 10^{-2}$
- $2.0 \times 10^{-2}$



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**a digital pH meter**

A blue color will result when bromthymol blue is added to an aqueous solution of:

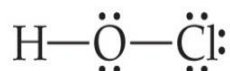
- $\text{NH}_4\text{Cl}$
- $\text{KHSO}_4$
- $\text{AlCl}_3$
- $\text{KH}_2\text{PO}_4$
- $\text{Na}_2\text{HPO}_4$

	pH range for color change								
	0	2	4	6	8	10	12	14	
Methyl violet	Yellow			Violet					
Thymol blue		Red			Yellow			Blue	
Methyl orange			Red			Yellow			
Methyl red				Red			Yellow		
Bromthymol blue				Yellow			Blue		
Phenolphthalein					Colorless			Pink	
Alizarin yellow R						Yellow			Red

# What is the pH of a 0.010 M HClO<sub>4</sub> solution ?

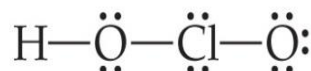
- < 1
- 1
- 2
- 7
- > 7

Hypochlorous



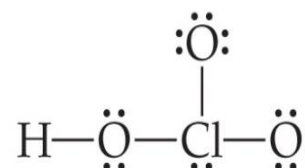
$$K_a = 3.0 \times 10^{-8}$$

Chlorous



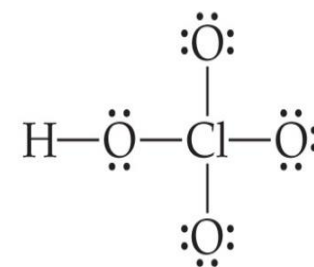
$$K_a = 1.1 \times 10^{-2}$$

Chloric



Strong acid

Perchloric



Strong acid



Increasing acid strength

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What is the pH of a 0.010 M HF solution ?

- < 1
- 1
- 2
- > 2
- 7

# Which acid is the strongest ?

- $\text{H}_2\text{S}$
- $\text{HF}$
- $\text{HCl}$
- $\text{HBr}$
- $\text{HI}$

3A 13	4A 14	5A 15	6A 16	7A 17	8A 18 2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
113	114	115	116		

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# Which base is the strongest ?

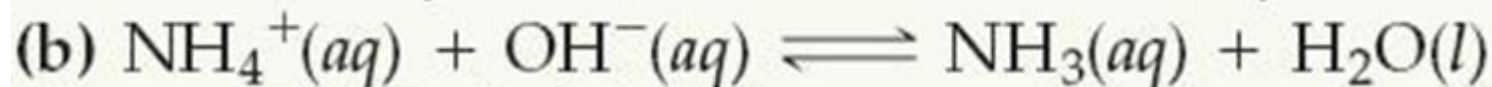
- $\text{ClO}_4^-$
- $\text{BrO}_3^-$
- $\text{BrO}_4^-$
- $\text{IO}_3^-$
- $\text{IO}_4^-$

	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
	5 B	6 C	7 N	8 O	9 F	10 Ne
	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
	113	114	115	116		

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

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

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



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



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

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

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

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

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

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

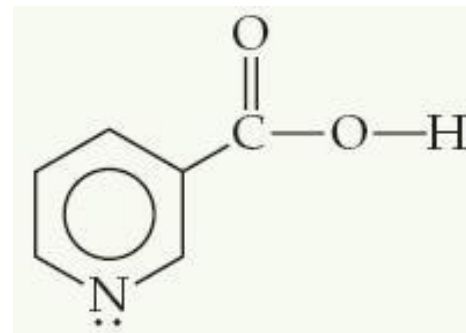
An aqueous solution of  $\text{HNO}_3$  has a pH of 2.34. What is the concentration of the acid?

*Answer: 0.0046 M*

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?

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

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

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

*Answer: 2.7%*

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

***Answer: 3.41***



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

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

- (a)** Calculate the pH of a 0.020 *M* solution of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ). (See Table 16.3 for  $K_{a1}$  and  $K_{a2}$ .)
- (b)** Calculate the concentration of oxalate ion  $[\text{C}_2\text{O}_4^{2-}]$ , in this solution.

***Answers:*** (a) pH = 1.80 ,

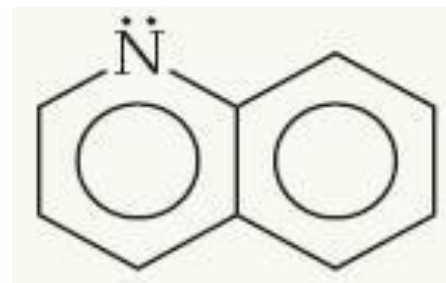
(b)  $[\text{C}_2\text{O}_4^{2-}] = 6.4 \times 10^{-5} \text{ M}$

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

*Answer: 0.12 M*

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

(b) The base quinoline has the following structure: Its conjugate acid is listed in handbooks as having a  $\text{p}K_a$  of 4.90. What is the base dissociation constant for quinoline?



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

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

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

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

*Answer: acidic*

