Chapter 16
Acid-Base Equilibria

16.1 Acids and Bases: A Brief Review

Properties of Acids & Bases

Acids:

Sour taste

pH less than 7

Litmus paper – red

Phenolphthalein - clear

Bases

Bitter taste

Slippery

pH greater than 7

Litmus paper – blue

Phenolphthalein - pink

Arrhenius Definition of Acid & Base

Svante Arrhenius

An **acid** is a substance that, when dissolved in water, increases the concentration of hydrogen ions.

A **base** is a substance that, when dissolved in water, increases the concentration of hydroxide ions.

16.1 Give It Some Thought

Which two ions are central to the Arrhenius definitions of acids and bases?

16.2 Brønsted-Lowry Acids and Bases

Bronsted-Lowry Definition of Acid & Base

Johannes Brønsted & Thomas Lowry

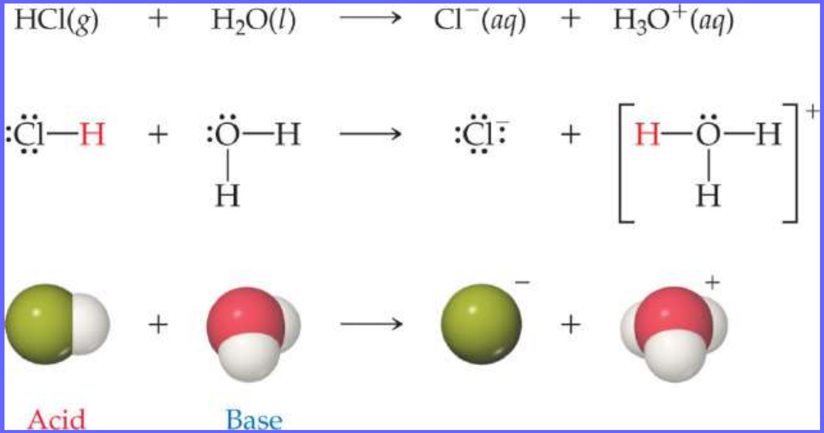
An **acid** is a proton donor.

A **base** is a proton acceptor.

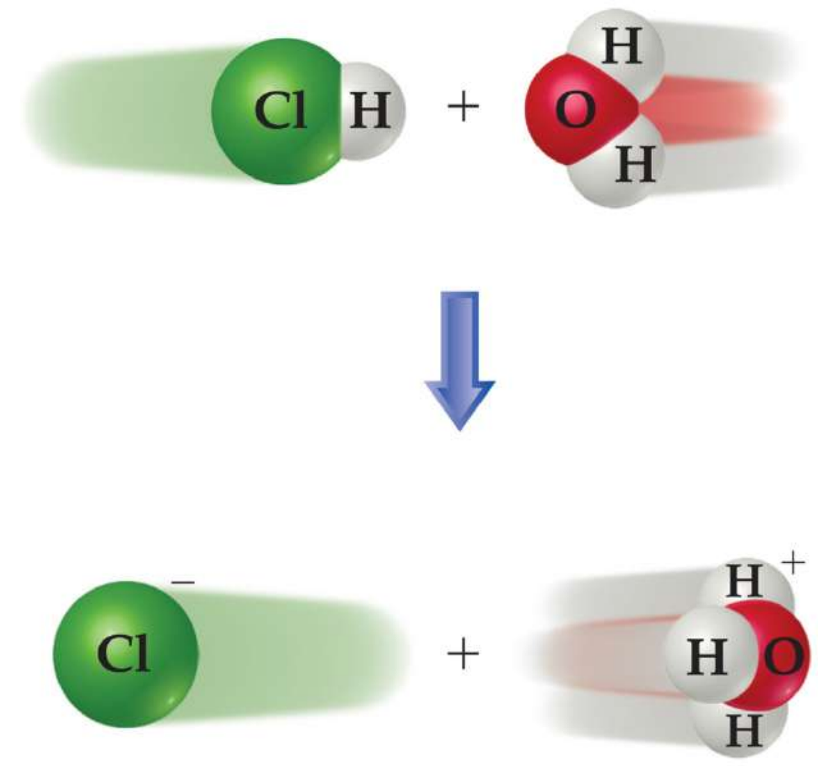
Brønsted–Lowry Acid and Base

A Brønsted–Lowry **acid** must have at least one removable (acidic) proton (H^+) to donate.

A Brønsted–Lowry **base** must have at least one nonbonding pair of electrons to accept a proton (H^+).



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.

What Is Different about Water?

Water can act as a Brønsted–Lowry base and accept a proton (H^+) from an acid, as on the previous slide.

It can also donate a proton and act as an acid, as is seen below.

This makes water **amphiprotic**.

$$\underset{\text{Base}}{NH_3(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

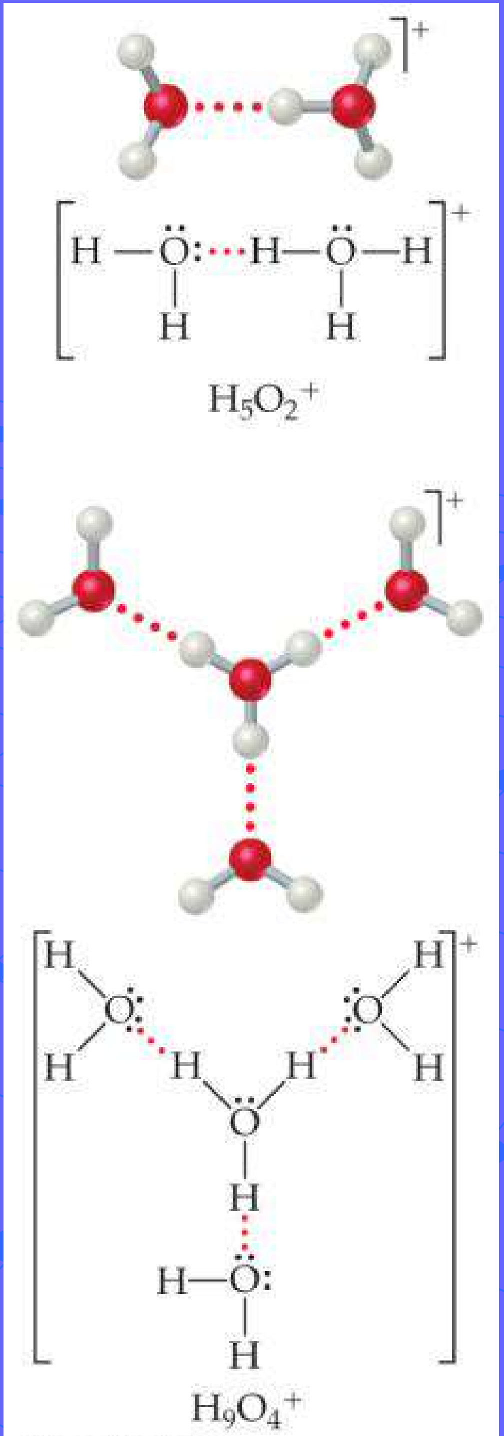
Which type of intermolecular force do the dotted lines in this figure represent?

a. Hydrogen bond

b. Dispersion bond

c. Covalent bond

d. Ionic bond



16.2 Give It Some Thought

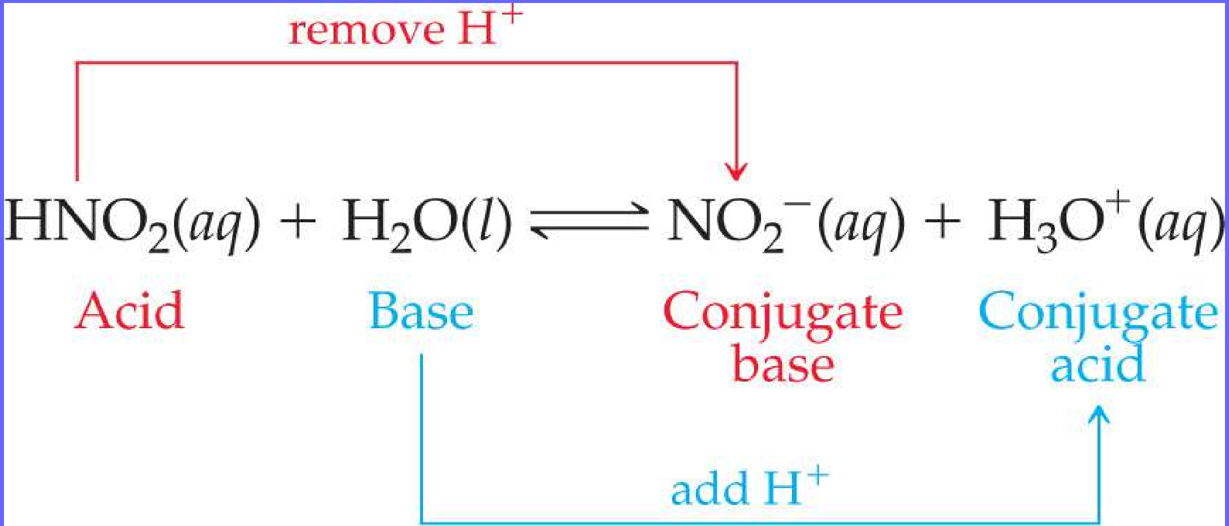
In the forward reaction, which substance acts as the Bronsted-Lowry base:

$HSO_4^-(aq) + NH_3(aq) \leftrightarrow SO_4^{2-}(aq) + NH_4^+(aq)$?

Conjugate Acids and Bases

The term **conjugate** means “joined together as a pair.”

Reactions between acids and bases always yield their conjugate bases and acids.



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

Example

Determine the conjugate acid-base pairs in each reaction:

$NH_4^+(aq) + CN^-(aq) \rightleftarrows HCN(aq) + NH_3(aq)$

$(CH_3)_3N(aq) + H_2O(l) \rightleftarrows (CH_3)_3NH^+(aq) + OH^-(aq)$

$HCHO_2(aq) + PO_4^{3-}(aq) \rightleftarrows CHO_2^-(aq) + HPO_4^{2-}(aq)$

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^-

Practice Exercise 1

Consider the following equilibrium reaction:

$$HSO_4^- (aq) + OH^- (aq) \leftrightarrow SO_4^{2-} (aq) + H_2O(l)$$

Which substances are acting as acids in the reaction?

(a) HSO_4^- and OH^-

(b) HSO_4^- and H_2O

(c) OH^- and SO_4^{2-}

(d) SO_4^{2-} and H_2O

(e) None

Practice Exercise 2

Write the formula for the conjugate acid of each of the following:

HSO_3^-

F^-

PO_4^{3-}

CO

Sample Exercise 16.2 Writing Equations for Proton–Transfer Reactions

The hydrogen sulfite ion (HSO_3^-) is amphiprotic.

(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.

Practice Exercise 1

The dihydrogen phosphate ion, $H_2PO_4^-$, is amphiprotic. In which of the following reactions is this ion serving as a base?

(i) $H_3O^+(aq) + H_2PO_4^-(aq) \leftrightarrow H_3PO_4(aq) + H_2O(l)$

(ii) $H_3O^+(aq) + HPO_4^{2-}(aq) \leftrightarrow H_2PO_4^-(aq) + H_2O(l)$

(iii) $H_3PO_4(aq) + HPO_4^{2-}(aq) \leftrightarrow 2\ H_2PO_4^-(aq)$

(a) i only

(b) i and ii

(c) i and iii

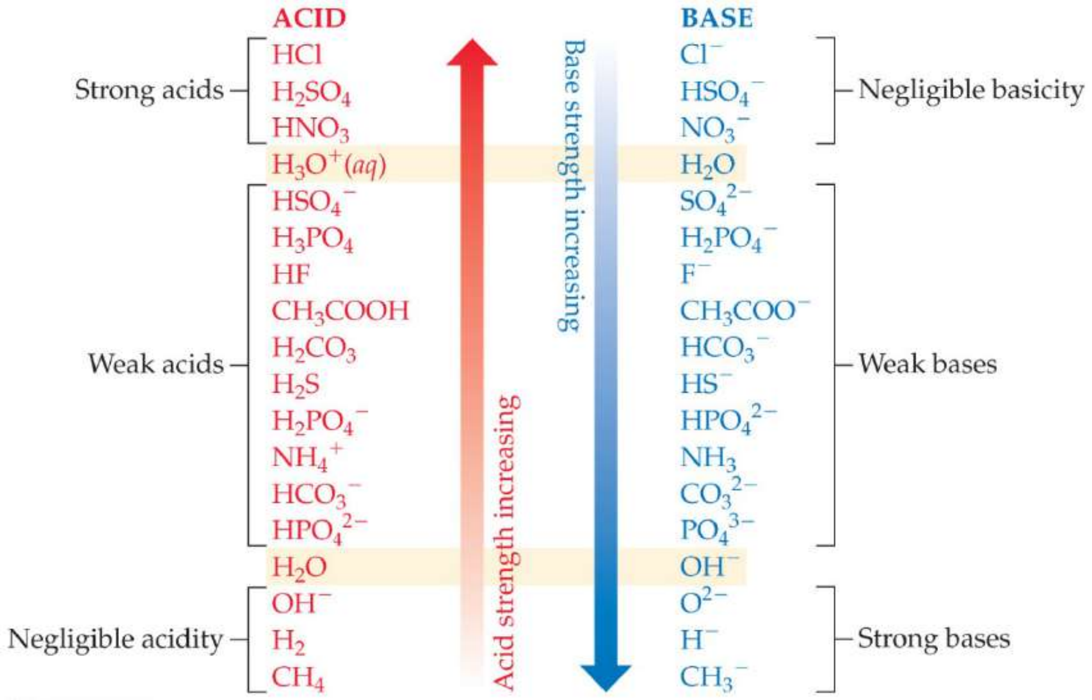
(d) ii and iii

(e) i, ii, and iii

Relative Strengths of Acids and Bases

Acids above the line with H_2O as a base are *strong acids*; their conjugate bases do *not* act as acids in water.

Bases below the line with H_2O as an acid are *strong bases*; their conjugate acids do *not* act as acids in water.



	ACID	**BASE**	
Strong acids	HCl	Cl^-	Negligible basicity
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak acids	HSO_4^-	SO_4^{2-}	Weak bases
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	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 acidity	OH^-	O^{2-}	Strong bases
	H_2	H^-	
	CH_4	CH_3^-	

- The substances between the lines with H_2O are conjugate acid–base pairs in water.

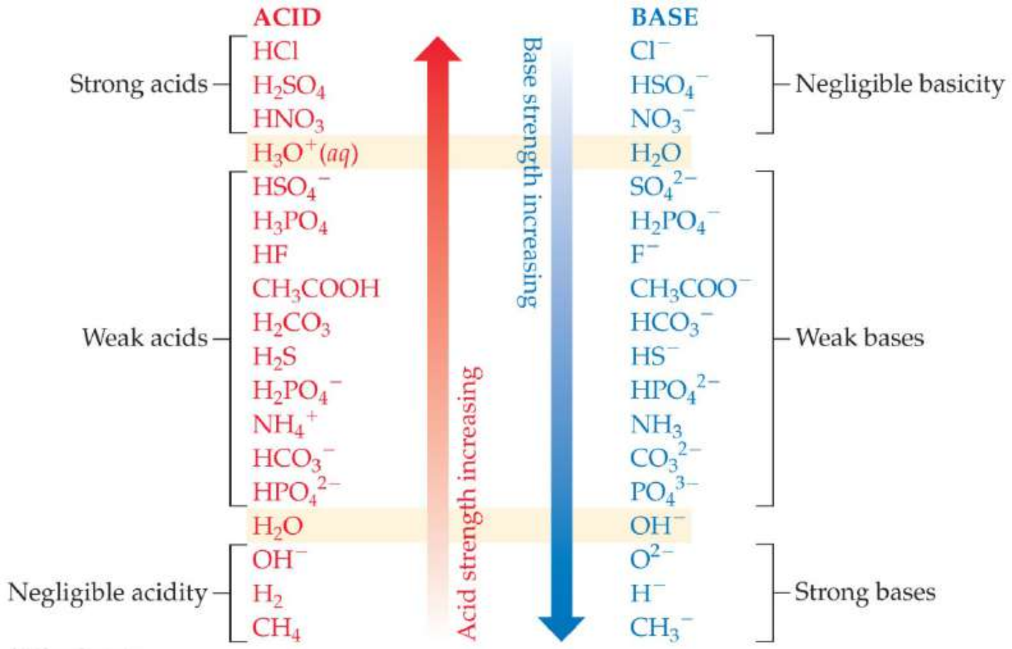
If O^{2-} ions are added to water, what reaction, if any, occurs?

a. No reaction

b. $O^{2-}(aq) + H^{+}(aq) \rightarrow HO^{2-}(aq)$

c. $O^{2-}(aq) + 2H^{+}(aq) \rightarrow H_2O_2(aq)$

d. $O^{2-}(aq) + H_2O(aq) \rightarrow 2OH^{-}(aq)$



	ACID	BASE	
Strong acids	HCl	Cl^-	Negligible basicity
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak acids	HSO_4^-	SO_4^{2-}	Weak bases
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	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 acidity	OH^-	O^{2-}	Strong bases
	H_2	H^-	
	CH_4	CH_3^-	

Acid and Base Strength

In every acid–base reaction, equilibrium favors transfer of the proton from the stronger acid to the stronger base to form the weaker acid and the weaker 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 far to the right ($K >> 1$).
- $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$
- Acetate is a stronger base than H_2O, so the equilibrium favors the left side ($K < 1$).

16.2 Give It Some Thought

Given that $HClO_4$ is a strong acid, how would you classify the basicity of ClO_4^-?

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 ($K_c > 1$):

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

Practice Exercise 1

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

(i) $CH_3COOH(aq) + HS^-(aq) \leftrightarrow CH_3COO^-(aq) + H_2S(aq)$

(ii) $F^-(aq) + NH_4^+(aq) \leftrightarrow HF(aq) + NH_3(aq)$

(iii) $H_2CO_3(aq) + Cl^-(aq) \leftrightarrow HCO_3^-(aq) + HCl(aq)$

(a) i < ii < iii

(b) ii < i < iii

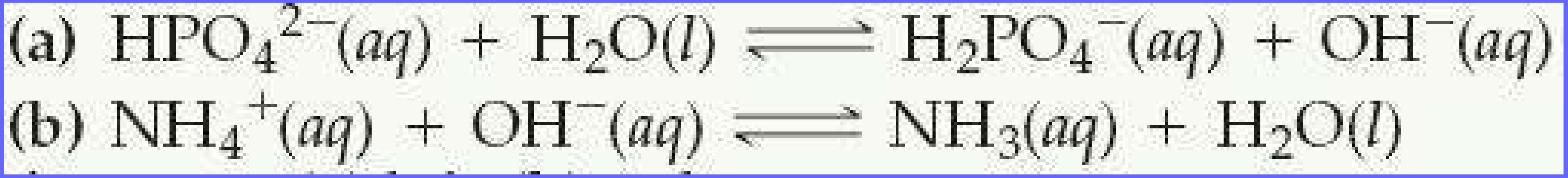
(c) iii < i < ii

(d) ii < iii < i

(e) iii < ii < i

Practice Exercise 2

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

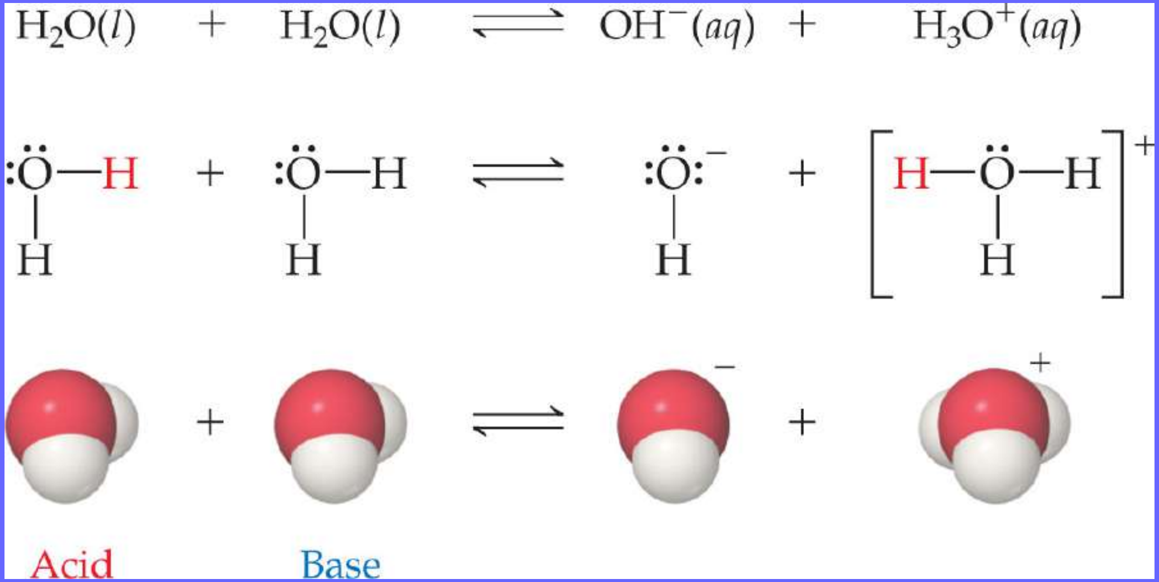
16.3 The Autoionization of Water

Autoionization of Water

Water is amphoteric.

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

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, $K_w = 1.0 \times 10^{-14}$

Aqueous Solutions Can Be Acidic, Basic, or Neutral

If a solution is neutral, $[H^+] = [OH^-]$.

If a solution is acidic, $[H^+] > [OH^-]$.

If a solution is basic, $[H^+] < [OH^-]$.

Acidic solution

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

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

Neutral solution

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

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

Basic solution

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

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

Suppose that equal volumes of the middle and right samples in the figure were mixed. Would the resultant solution be acidic, neutral, or basic?

a.Acidic

b.Neutral

c.Basic

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

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

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

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

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

Practice Exercise 1

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

(a) 1.0×10^{-8} *M*

(b) 1.0×10^{-7} *M*

(c) 1.0×10^{-6} *M*

(d) 1.0×10^{-2} *M*

(e) 1.0×10^{-9} *M*

Practice Exercise 2

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

(a) $[H^+] = 4 \times 10^{-9}\ M$

(b) $[OH^-] = 1 \times 10^{-7}\ M$

(c) $[OH^-] = 1 \times 10^{-13}\ M$

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

Calculate the concentration of $H^+(aq)$ in

(a) a solution in which $[OH^-]$ is 0.010 *M*

(b) a solution in which $[OH^-]$ is 1.8×10^{-9} *M*

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

Practice Exercise 1

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

(a) 2.5×10^{-8} *M*

(b) 4.0×10^{-8} *M*

(c) 2.5×10^{-7} *M*

(d) 2.5×10^{-6} *M*

(e) 4.0×10^{-6} *M*

Practice Exercise 2

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

(a) $[H^+] = 2 \times 10^{-6}\ M$

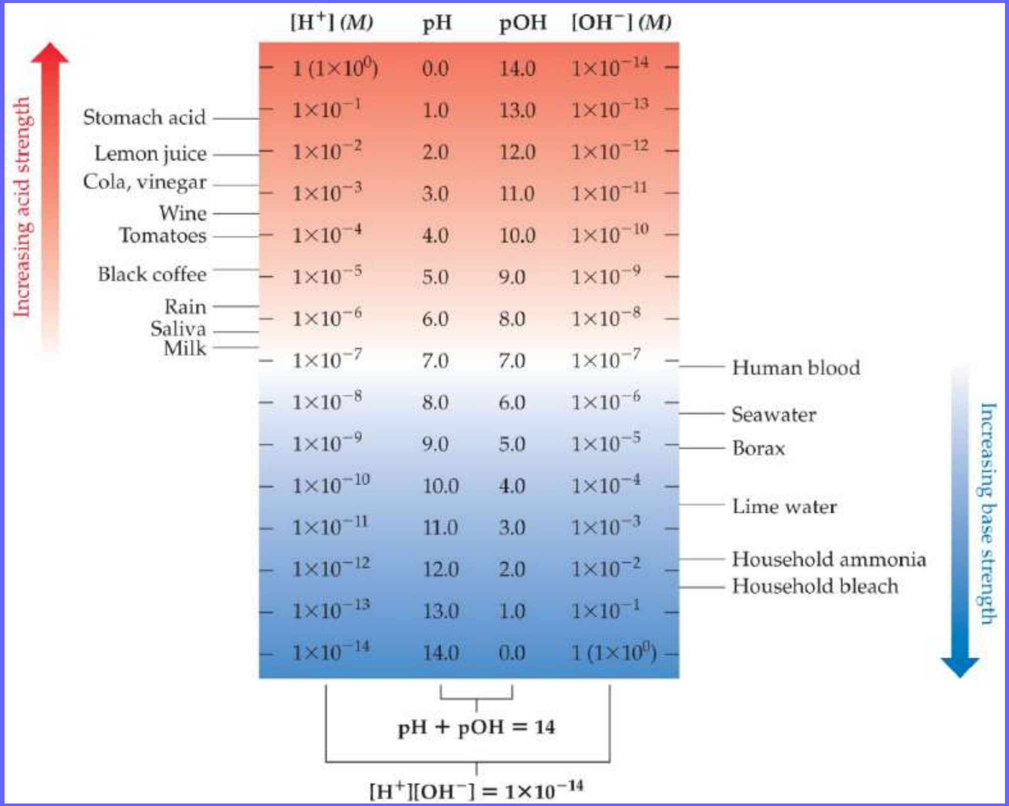
(b) $[H^+] = [OH^-]$

(c) $[H^+] = 200 \times [OH^-]$

16.4 The pH Scale

pH

- pH is a method of reporting hydrogen ion concentration.
- pH = –log[H$^+$]
- Neutral pH is 7.00.
- Acidic pH is below 7.00.
- Basic pH is above 7.00.



$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*M*)
$1\ (1\times10^{0})$	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	$1\ (1\times10^{0})$

pH + pOH = 14

$[H^+][OH^-] = 1\times10^{-14}$

16.4 Give It Some Thought

Is it possible for a solution to have a negative pH? If so, would that pH signify a basic or acidic solution?

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

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

(a) a solution in which $[OH^-]$ is 0.010 *M*

(b) a solution in which $[OH^-]$ is 1.8×10^{-9} *M*

Practice Exercise 1

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

(a) 0.83

(b) 2.2

(c) 2.17

(d) 11.83

(e) 12

Practice Exercise 2

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

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

Other “p” Scales

The “p” in pH tells us to take the –log of a quantity (in this case, hydrogen ions).

Some other “p” systems are

- pOH: $-\log[OH^-]$
- pK_w: $-\log K_w$

Relating pH and pOH

Because

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

we can take the –log of the equation

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

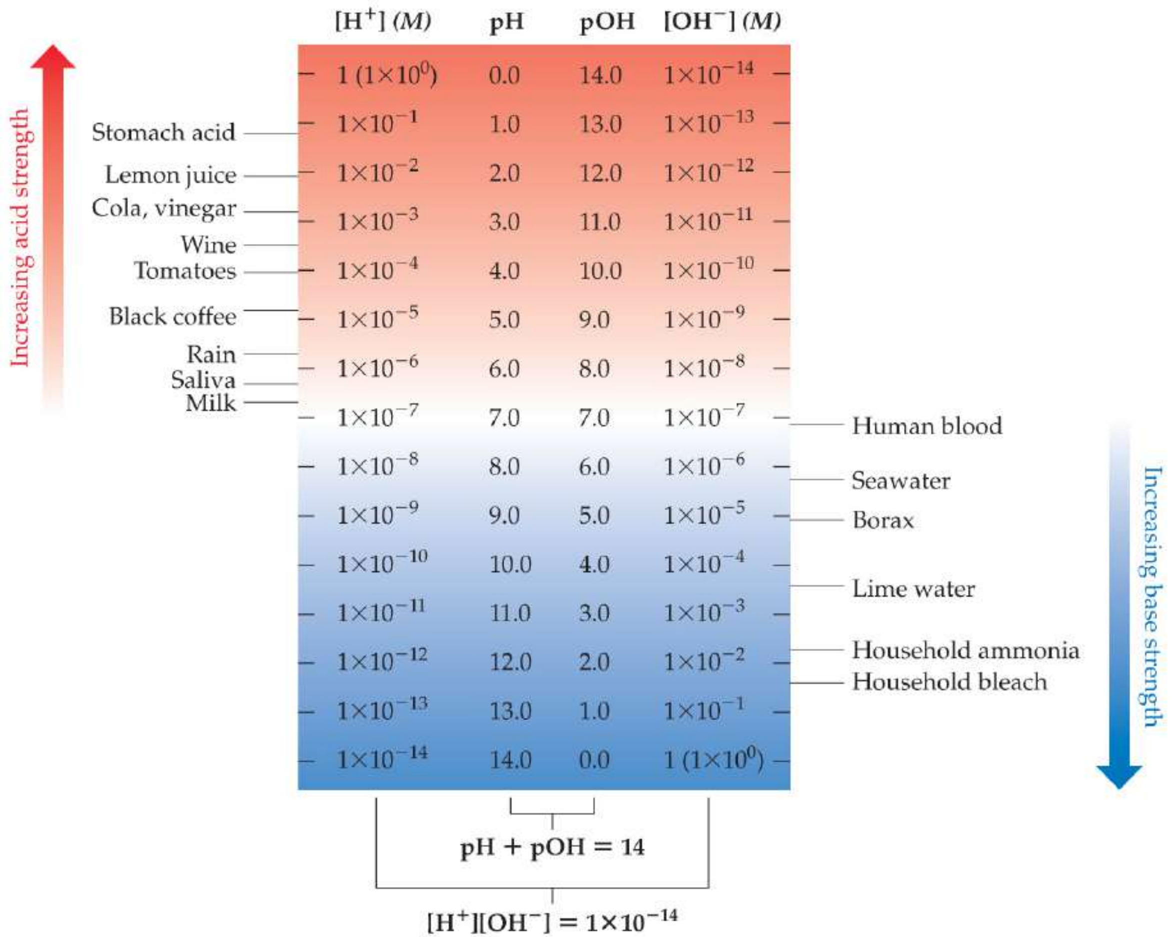
which results in

$$pH + pOH = pK_w = 14.00$$

Which is more acidic, black coffee or lemon juice?

a. Black coffee

b.Lemon juice



$[H^+]$ (*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})

$$pH + pOH = 14$$

$$[H^+][OH^-] = 1\times10^{-14}$$

16.4 Give It Some Thought

If the pOH for the solution is 3.00, what is the pH? Is the solution acidic or basic?

Sample Exercise 16.7

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

Practice Exercise 1

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

(i) The solution is acidic.

(ii) The pH of the solution is 14.00 – 10.53.

(iii) For this solution, $[OH^-] = 10^{-10.53}$ *M*.

(a) Only one of the statements is true.

(b) Statements (i) and (ii) are true.

(c) Statements (i) and (iii) are true.

(d) Statements (ii) and (iii) are true.

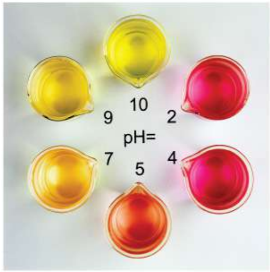
(e) All three statements are true.

Practice Exercise 2

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

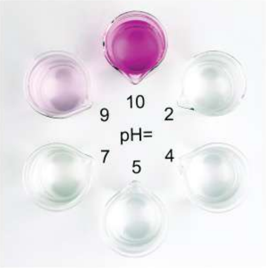
How Do We Measure pH?

Indicators, including litmus paper, are used for less accurate measurements; an indicator is one color in its acid form and another color in its basic form.



Methyl red

Bromthymol blue



Phenolphthalein

pH meters are used for accurate measurement of pH; electrodes indicate small changes in voltage to detect pH.

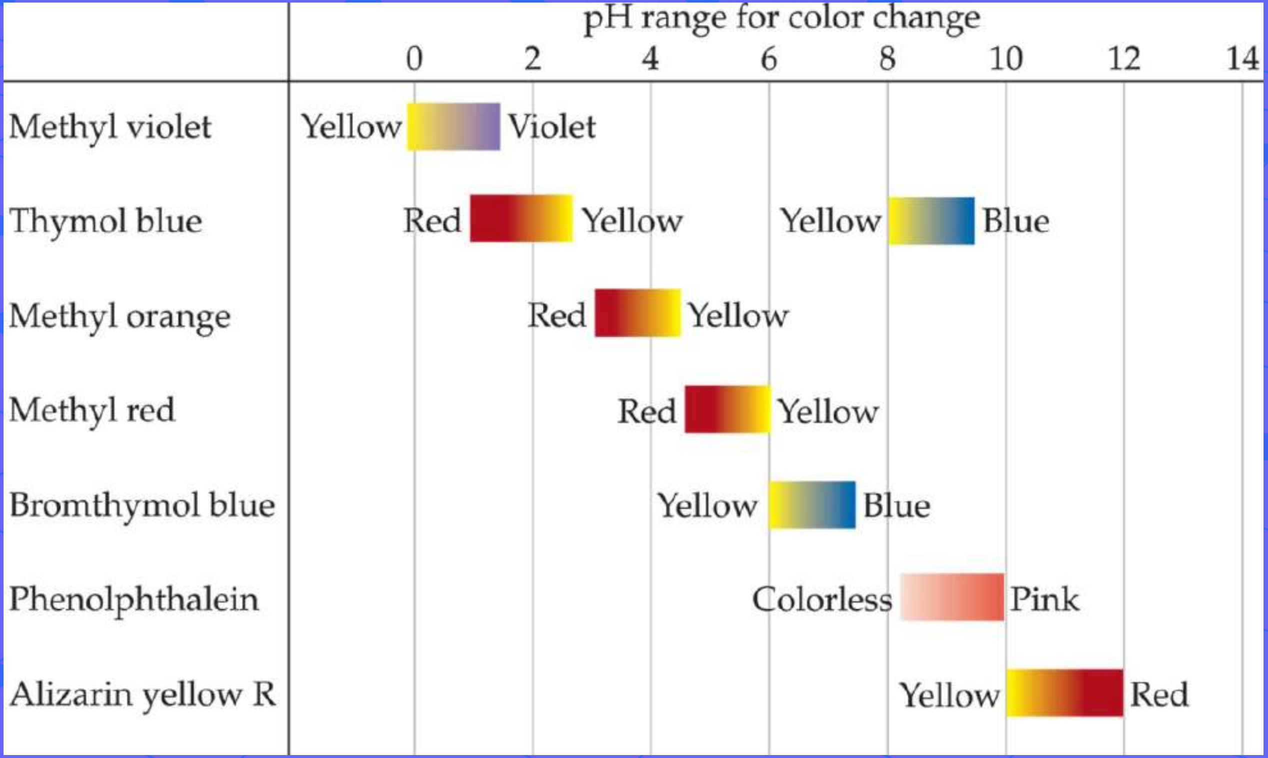
If a colorless solution turns pink when we add phenolphthalein, what can we conclude about the pH of the solution?

a. pH is near 7.

b. pH is < 7.

c. pH is > 10.

d. pH is > 12.



Which of these indicators is best suited to distinguish between a solution that is slightly acidic and one that is slightly basic?

a.Thymol blue

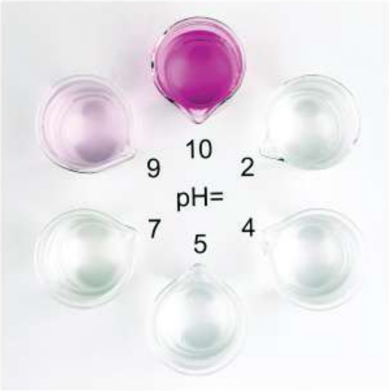
b.Bromothymol blue

c.Phenophthalein

d.Yellow blue

Methyl red

Bromthymol blue



Phenolphthalein

16.5 Strong Acids and Bases

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; e.g.,

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

So, for the monoprotic strong acids,

$[H_3O^+] = [\text{acid}]$

Sample Exercise 16.8 Calculating the pH of a Strong Acid

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

Practice Exercise 1

Order the following three solutions from smallest to largest pH:

(i) 0.20 *M* $HClO_3$

(ii) 0.0030 *M* HNO_3

(iii) 1.50 *M* HCl

(a) i < ii < iii

(b) ii < i < iii

(c) iii < i < ii

(d) ii < iii < i

(e) iii < ii < i

Practice Exercise 2

An aqueous solution of HNO_3 has a pH of 2.34. What is the concentration of the 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; e.g.,

$MOH(aq) \rightarrow M^{+}(aq) + OH^{-}(aq)$ *or*

$M(OH)_2(aq) \rightarrow M^{2+}(aq) + 2\ OH^{-}(aq)$

16.5 Give It Some Thought

Which solution has a higher pH, a 0.001 M solution of NaOH or a 0.001 M solution of $Ba(OH)_2$?

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 $Ca(OH)_2$?

Practice Exercise 1

Order the following three solutions from smallest to largest pH:

(i) 0.030 *M* $Ba(OH)_2$

(ii) 0.040 *M* KOH

(iii) pure water

(a) i < ii < iii

(b) ii < i < iii

(c) iii < i < ii

(d) ii < iii < i

(e) iii < ii < i

Practice Exercise 2

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

16.5 Give It Some Thought

The CH_3^- ion is the conjugate base of CH_4, and CH_4 shows no evidence of being an acid in water. Write a balanced equation for the reaction of CH_3^- and water.

Calculate pH involving strong acids & bases

0.425 g of $HClO_4$ in 2.00 L of solution

10.0 mL of 0.0105 M $Ca(OH)_2$ diluted to 500.0 mL

A mixture formed by adding 50.0 mL of 0.020 M HCl to 150 mL of 0.010 M HI

A solution formed by mixing 10.0 mL of 0.015 M $Ba(OH)_2$ with 40.0 mL of 7.5×10^{-3} M NaOH

16.6 Weak Acids

Weak Acids

For a weak acid, the equation for its dissociation is

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

Since it is an equilibrium, there is an equilibrium constant related to it, called the **acid-dissociation constant**, K_a: $K_a = [H_3O^+][A^-] / [HA]$

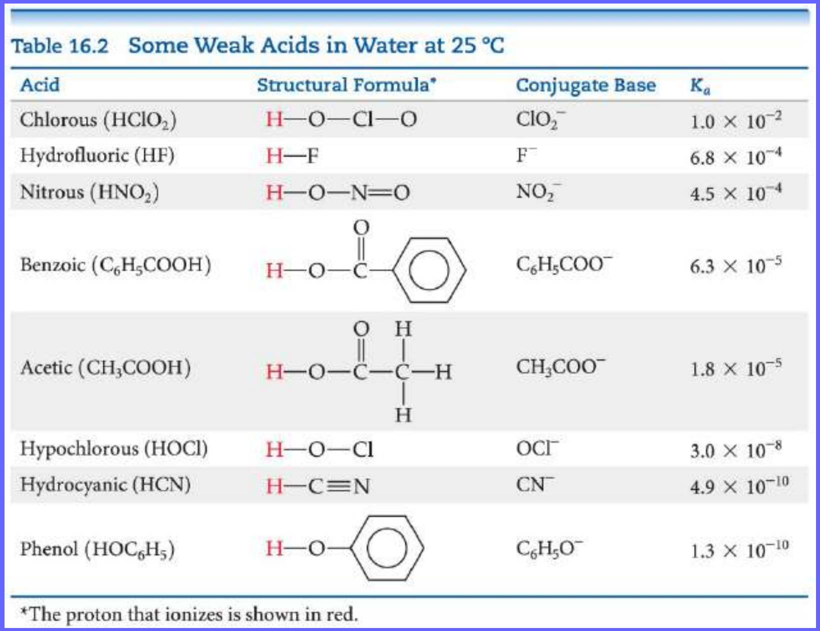


Table 16.2 Some Weak Acids in Water at 25 °C

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

*The proton that ionizes is shown in red.

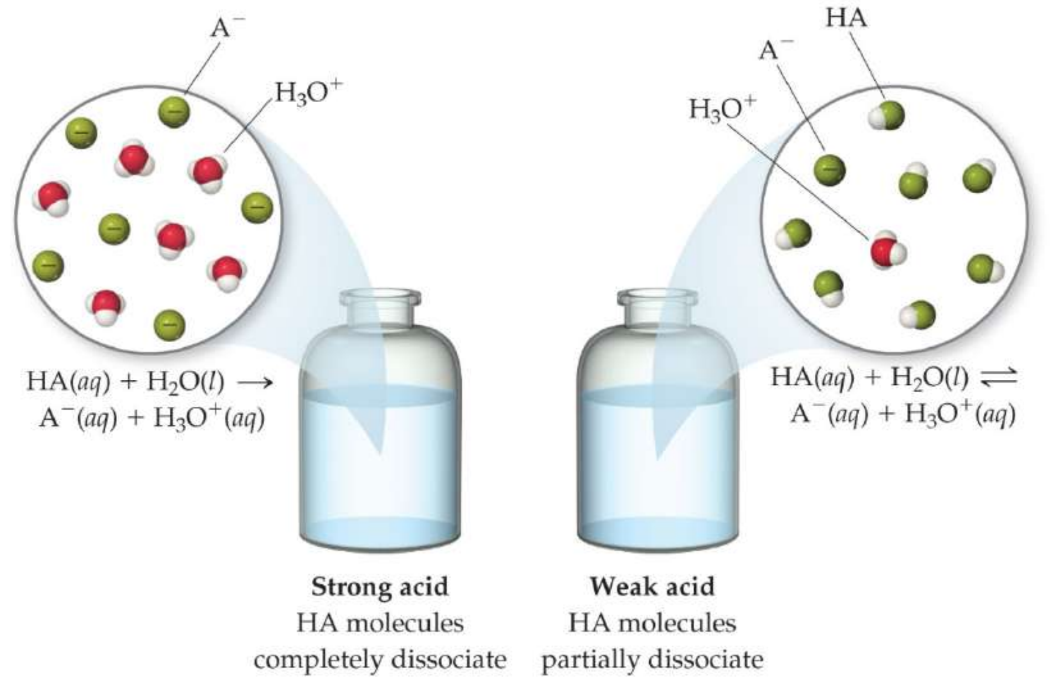
- The greater the value of K_a, the stronger is the acid.

Comparing Strong and Weak Acids

What is present in solution for a strong acid versus a weak acid?

Strong acids *completely* dissociate to ions.

Weak acids only *partially* dissociate to ions.



Strong acid
HA molecules
completely dissociate

Weak acid
HA molecules
partially dissociate

16.6 Give It Some Thought

Based on the entries in Table 16.2, which element is most commonly bonded to the acidic hydrogen?

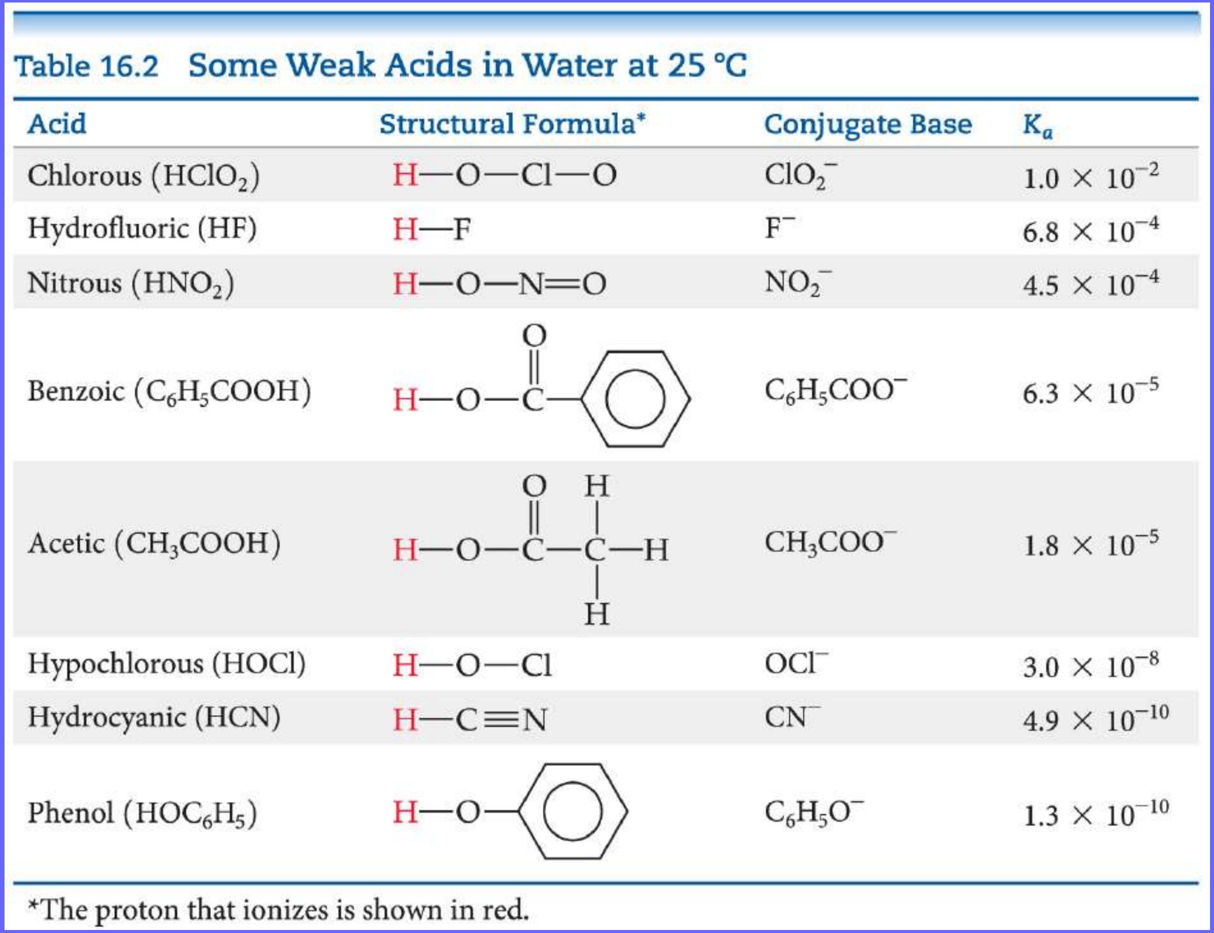


Table 16.2 Some Weak Acids in Water at 25 °C

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

*The proton that ionizes is shown in red.

Sample Exercise 16.10

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

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

- 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.
- $[H_3O^+] = [HCOO^-] = 10^{-2.38} = 4.2 \times 10^{-3}$

Calculating K_a from pH

Now we can set up a table for equilibrium concentrations. We know initial HCOOH (0.10 *M*) and ion concentrations (0 *M*); we found equilibrium ion concentrations (4.2×10^{-3} *M*); so we calculate the change, then the equilibrium HCOOH concentration.

	[HCOOH], *M*	$[H_3O^+]$, *M*	$[HCOO^-]$, *M*
Initially	0.10	0	0
Change	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
At equilibrium	$0.10 - 4.2 \times 10^{-3}$ $= 0.0958 = 0.10$	4.2×10^{-3}	4.2×10^{-3}

Calculating K_a from pH

- This allows us to calculate K_a by putting in the equilibrium concentrations.

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

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

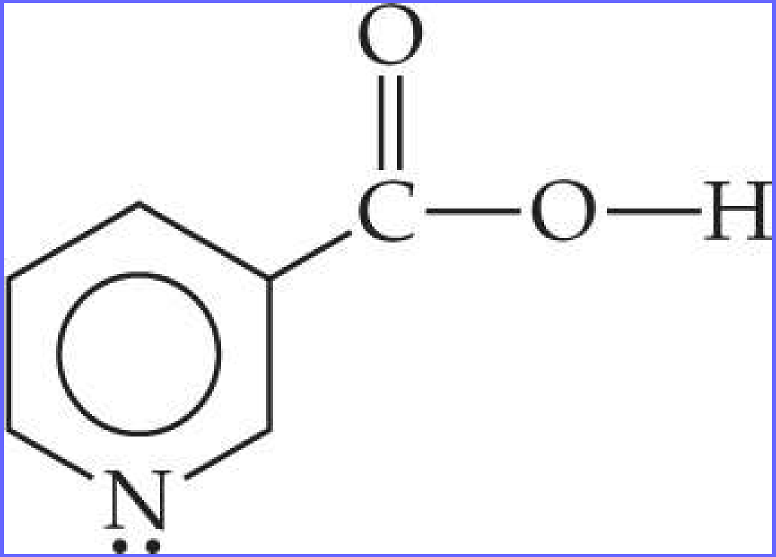
Practice Exercise 1

A 0.50 M solution of an acid HA has pH = 2.24. What is the value of K_a for the acid?

(a) 1.7×10^{-12}
(b) 3.3×10^{-5}
(c) 6.6×10^{-5}
(d) 5.8×10^{-3}
(e) 1.2×10^{-2}

Practice Exercise 2

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



A 0.020 *M* solution of niacin has a pH of 3.26. What is the acid-dissociation constant for niacin?

Calculating Percent Ionization & Sample Exercise 16.11

$$\text{Percent ionization} = \frac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100$$

In sample exercise 16.10,

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

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

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

$$= 4.2\%$$

Practice Exercise 1

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

(a) 0.090%

(b) 0.69%

(c) 0.90%

(d) 3.6%

(e) 9.0%

Practice Exercise 2

A 0.020 M solution of niacin has a pH of 3.26. Calculate the percent ionization of niacin (see practice exercise 2 from problem 16.10)

Method to Follow to Calculate pH Using K_a

1) Write the chemical equation for the ionization equilibrium.
2) Write the equilibrium constant expression.
3) Set up a table for Initial/Change in/Equilibrium Concentration to determine equilibrium concentrations as a function of change (x).
4) Substitute equilibrium concentrations into the equilibrium constant expression and solve for x. (Make assumptions if you can!)

Example

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

1) $HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$

2) $K_a = [H_3O^+][C_2H_3O_2^-] / [HC_2H_3O_2]$

3)

	CH_3COOH (*M*)	H_3O^+ (*M*)	CH_3COO^- (*M*)
Initial Concentration (*M*)	0.30	0	0
Change in Concentration (*M*)	$-x$	$+x$	$+x$
Equilibrium Concentration (*M*)	$0.30 - x$	x	x

Example (concluded)

4) $K_a = [H_3O^+][C_2H_3O_2^-] / [HC_2H_3O_2]$

$= (x)(x) / (0.30 - x)$

If we assume that $x << 0.30$, then $0.30 - x$ becomes 0.30. The problem becomes easier, since we don't have to use the quadratic formula to solve it.

$K_a = 1.8 \times 10^{-5} = x^2 / 0.30$, so $x = 2.3 \times 10^{-3}$

$x = [H_3O^+]$, so $\text{pH} = -\log(2.3 \times 10^{-3}) = 2.64$

16.6 Give It Some Thought

Would a 1.0×10^{-8} M solution of HCl have a pH < 7, pH = 7, or pH > 7?

Sample Exercise 16.12

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

Practice Exercise 1

What is the pH of a 0.40 *M* solution of benzoic acid, C_6H_5COOH? (K_a = 6.3 x 10^{-5})

(a) 2.30

(b) 2.10

(c) 1.90

(d) 4.20

(e) 4.60

Practice Exercise 2

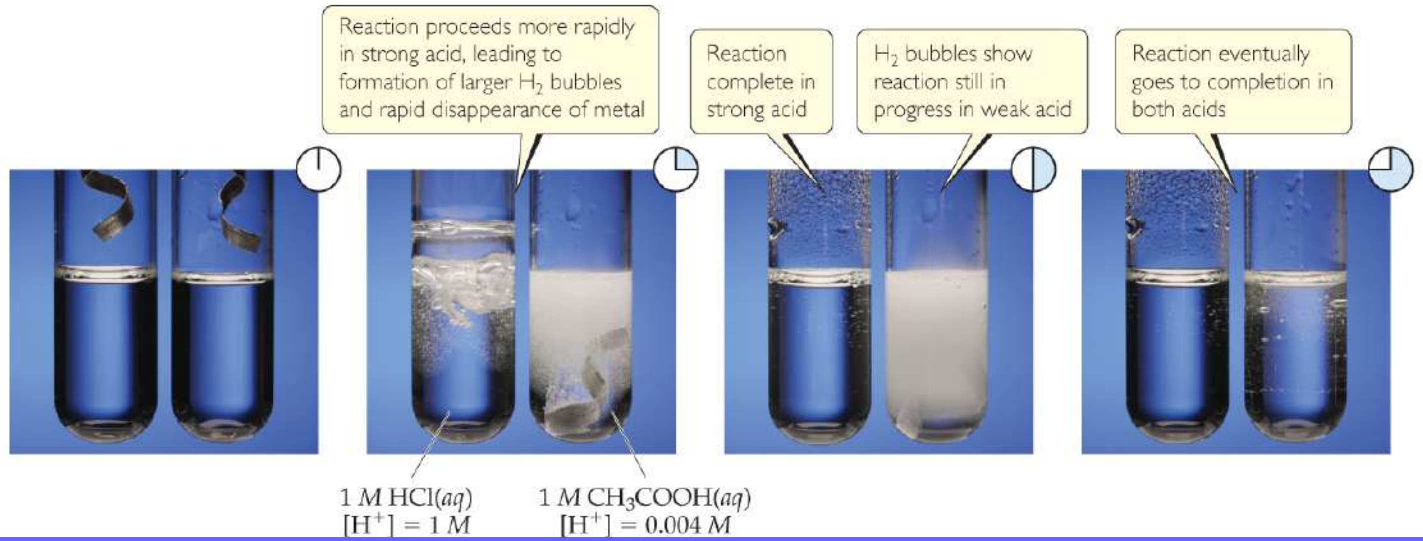
The K_a for niacin is 1.5 × 10^{-5}. What is the pH of a 0.010 *M* solution of niacin?

Strong vs. Weak Acids—Another Comparison

Strong Acid: $[H^+]_{eq} = [HA]_{init}$

Weak Acid: $[H^+]_{eq} < [HA]_{init}$

This creates a difference in conductivity and in rates of chemical reactions.



Reaction proceeds more rapidly in strong acid, leading to formation of larger H_2 bubbles and rapid disappearance of metal

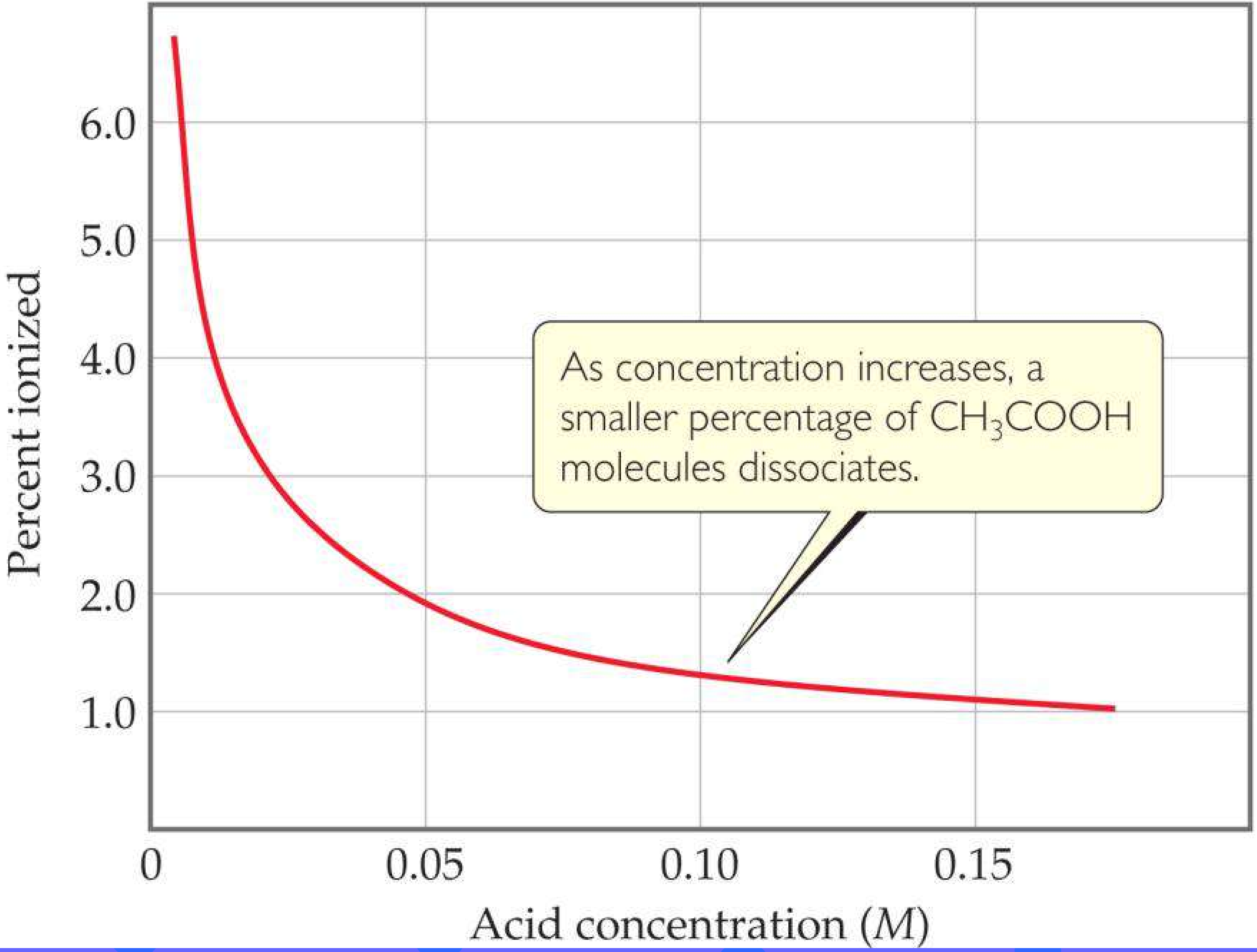
Reaction complete in strong acid

H_2 bubbles show reaction still in progress in weak acid

Reaction eventually goes to completion in both acids

$1\ M$ HCl(aq)
$[H^+] = 1\ M$

$1\ M$ CH_3COOH(aq)
$[H^+] = 0.004\ M$



As concentration increases, a smaller percentage of CH_3COOH molecules dissociates.

Is the trend observed in this graph consistent with Le Châtelier's principle? Explain.

a. No, as the CH_3COOH concentration increases, the following reaction should produce more product and thus increase the percent ionized: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$.

b. No, because K_a changes slightly as the concentration of CH_3COOH increases, and this permits the degree of ionization to change as shown on the graph.

c. Yes, changing the concentration of the acid in different solutions of CH_3COOH does not change the value of K_a; thus, LeChâtelier's principle is still valid.

d. Yes, the percent concentration must decrease as the concentration of CH_3COOH increases, otherwise the concentration of all three species would increase to ensure that K_a remains constant. The decrease in percent ionization with an increase in acid concentration offsets the fact that the rate of formation of the product is twice the rate of disappearance of the acid.

Sample Exercise 16.13

Calculate the pH and percentage of HF molecules ionized in a 0.10 *M* HF solution. ($K_a = 6.8 \times 10^{-4}$).

Practice Exercise 1

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

(a) 1.58

(b) 2.10

(c) 2.30

(d) 2.58

(e) 2.64

Practice Exercise 2

In Practice Exercise 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*.

Polyprotic Acids

Polyprotic acids have more than one acidic proton.

It is always easier to remove the first proton than any successive proton.

If the factor in the K_a values for the first and second dissociation has a difference of 3 or greater, the pH generally depends *only* on the first dissociation.

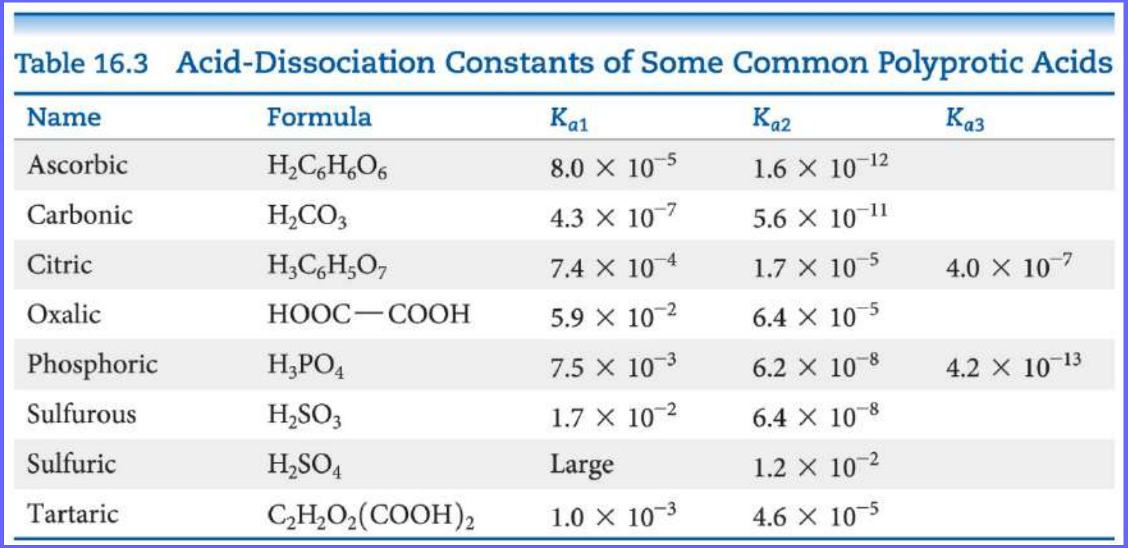


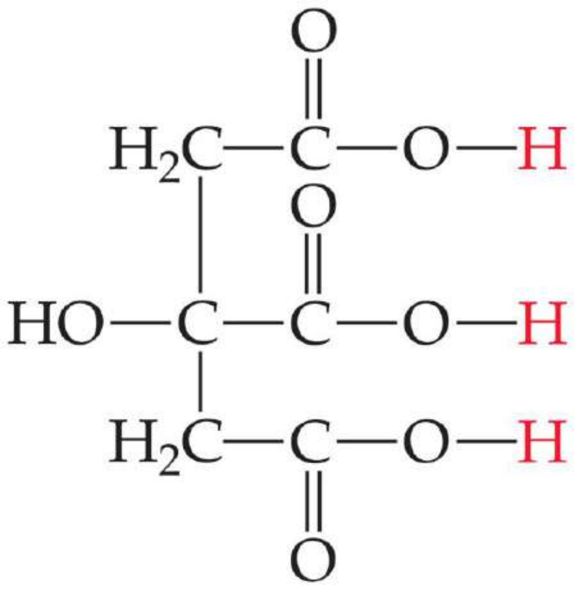
Table 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	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	HOOC—COOH	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$C_2H_2O_2(COOH)_2$	1.0×10^{-3}	4.6×10^{-5}	

16.6 Give It Some Thought

What is the equilibrium associated with K_{a3} for H_3PO_4?

Citric acid has four hydrogens bonded to oxygen. How does the hydrogen that is not an acidic proton differ from the other three?



Citric acid

a. A H bonded to a O—C— is more acidic tha shown in red.

b. A H bonded to a O—C— is only slightly the H atoms shown in red.

c. A H bonded (shown in red) to a O—C that is part of the —COOH (carboxylate) group is acidic but the H bonded to in the form of HO—C— (alcohol) group is not acidic.

d. A H bonded (shown in red) to a O—C that is part of the —COOH (carboxylate) group is acidic but the H bonded to in the form of HO—C— (alcohol) group is part of a basic group.

Sample Exercise 16.14 Calculating the pH of a Polyprotic Acid Solution

The solubility of CO_2 in pure water at 25 ºC and 0.1 atm pressure is 0.0037 *M*. The common practice is to assume that all of the dissolved CO_2 is in the form of carbonic acid (H_2CO_3), which is produced by reaction between the CO_2 and H_2O:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

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

Practice Exercise 1

What is the pH of a 0.28 *M* solution of ascorbic acid (Vitamin C)? ($K_{a1} = 8.0 \times 10^{-5}$ and $K_{a2} = 1.6 \times 10^{-12}$.)

(a) 2.04

(b) 2.32

(c) 2.82

(d) 4.65

(e) 6.17

Practice Exercise 2

(a) Calculate the pH of a 0.020 *M* solution of oxalic acid ($H_2C_2O_4$). (K_{a1} = 5.9 x 10^{-2} and K_{a2} = 6.4 x 10^{-5})

(b) Calculate the concentration of oxalate ion $[C_2O_4{}^{2-}]$, in this solution.

16.7 Weak Bases

Weak Bases

Ammonia, NH_3, is a weak base.

Like weak acids, weak bases have an equilibrium constant called the **base dissociation constant**.

Equilibrium calculations work the *same* as for acids, using the base dissociation constant instead.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Base Dissociation Constants

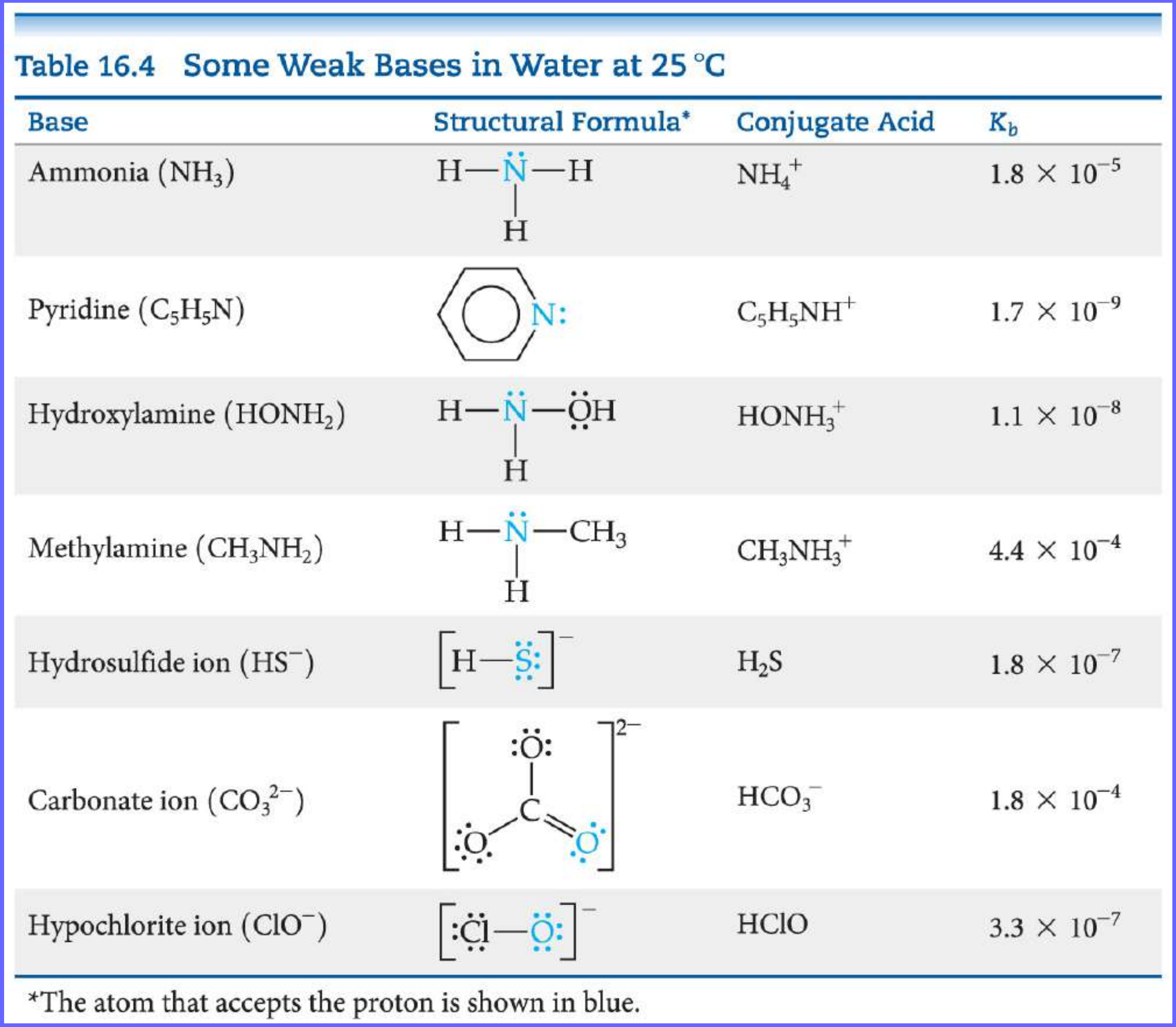


Table 16.4 Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)	$\begin{array}{c}\mathrm{H-\ddot{N}-H}\\ \vert\\ \mathrm{H}\end{array}$	NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine ($HONH_2$)	$\begin{array}{c}\mathrm{H-\ddot{N}-\ddot{\underset{..}{O}}H}\\ \vert\\ \mathrm{H}\end{array}$	$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)	$\begin{array}{c}\mathrm{H-\ddot{N}-CH_3}\\ \vert\\ \mathrm{H}\end{array}$	$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$\left[\mathrm{H-\ddot{\underset{..}{S}}:}\right]^-$	H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})	$\left[\begin{array}{ccc} & :\ddot{O}: & \\ & \vert & \\ & C & \\ :\ddot{\underset{..}{O}} & & \ddot{O}: \end{array}\right]^{2-}$	HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$\left[:\ddot{\underset{..}{Cl}}-\ddot{\underset{..}{O}}:\right]^-$	HClO	3.3×10^{-7}

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

Sample Exercise 16.15

What is the pH of 0.15 *M* NH_3?

1) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

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

3)

	NH_3 (*M*)	NH_4^+ (*M*)	OH^- (*M*)
Initial Concentration (*M*)	0.15	0	0
Change in Concentration (*M*)	$-x$	$+x$	$+x$
Equilibrium Concentration (*M*)	$0.15 - x$	x	x

Example (completed)

4) $1.8 \times 10 - 5 = x^2 / (0.15 - x)$

If we assume that $x \ll 0.15$, $0.15 - x = 0.15$.

Then: $1.8 \times 10^{-5} = x^2 / 0.15$

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

Note: x is the molarity of OH^-, so $-\log(x)$ will be the pOH (pOH = 2.80) and [14.00 – pOH] is pH (pH = 11.20).

Practice Exercise 1

What is the pH of a 0.65 *M* solution of pyridine, C_5H_5N? ($K_b = 1.7 \times 10^{-9}$.)

(a) 4.48

(b) 8.96

(c) 9.52

(d) 9.62

(e) 9.71

Practice Exercise 2

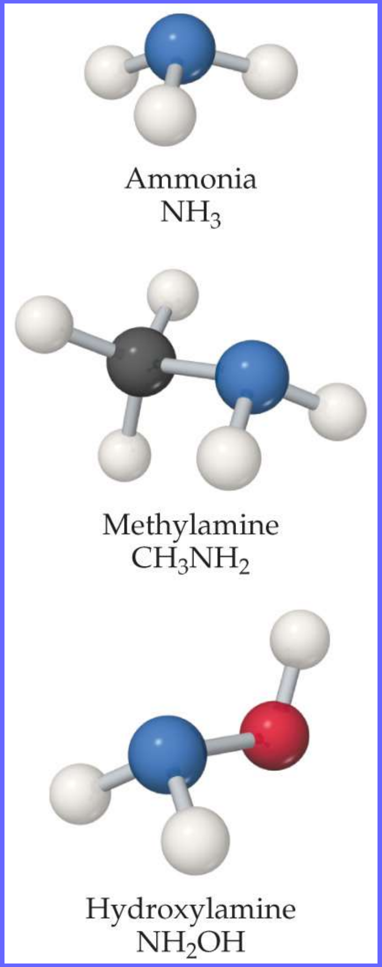
Which of the following compounds should produce the highest pH as a 0.05 M solution: pyradine ($K_b = 1.7 \times 10^{-9}$), methylamine ($K_b = 4.4 \times 10^{-4}$), or nitrous acid ($K_a = 4.5 \times 10^{-4}$)?

Types of Weak Bases

Two main categories

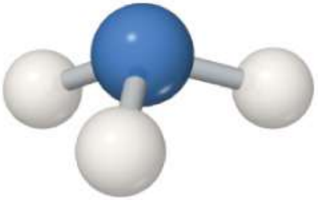
1) Neutral substances with an Atom that has a nonbonding pair of electrons that can accept H^+ (like ammonia and the **amines**)

2) Anions of weak acids

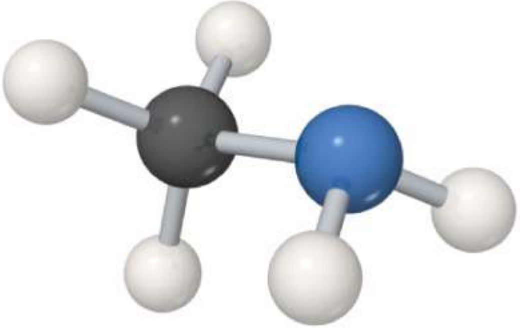


When hydroxylamine acts as base, which atom accepts the proton?

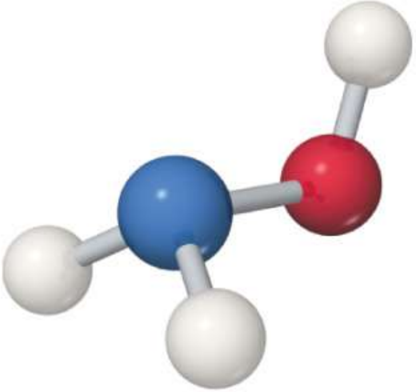
a. Carbon
b. Nitrogen
c. Hydrogen
d. Oxygen



Ammonia
NH_3



Methylamine
CH_3NH_2



Hydroxylamine
NH_2OH

Sample Exercise 16.16

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.

Practice Exercise 1

The benzoate ion, $C_6H_5COO^-$, is a weak base with $K_b = 1.6 \times 10^{-10}$. How many moles of sodium benzoate are present in 0.50 L of a solution of NaC_6H_5COO if the pH is 9.04?

(a) 0.38

(b) 0.66

(c) 0.76

(d) 1.5

(e) 2.9

Practice Exercise 2

A solution of NH_3 in water has a pH of 11.17. What is the molarity of the solution?

16.8 Relationship Between K_a and K_b

Relationship between K_a and K_b

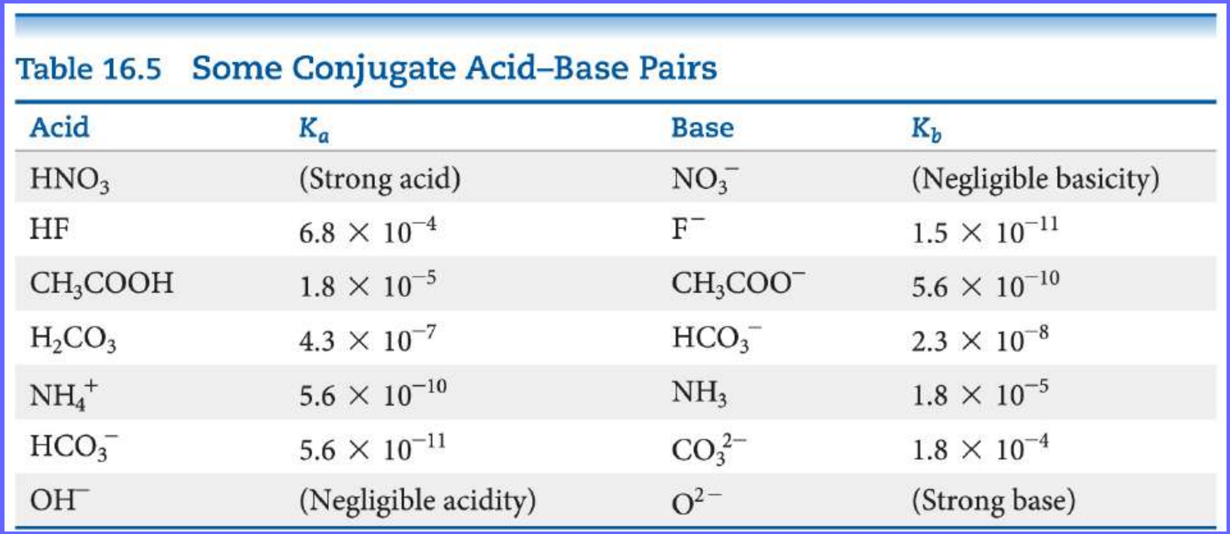


Table 16.5 Some Conjugate Acid–Base Pairs

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

For a conjugate acid–base pair, 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.

16.8 Give It Some Thought

K_a for acetic acid is 1.8×10^{-5}. What is the first digit of the pK_a value for acetic acid?

Sample Exercise 16.17

Calculate:

(a) the base-dissociation constant, K_b, for the fluoride ion (F^-), the K_a of HF is 6.8 x 10^{-4}

(b) the acid dissociation constant, K_a, for the ammonium ion (NH_4^+), the K_b of NH_3 is 1.8 x 10^{-5}.

Practice Exercise 1

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

(i) $(CH_3)_3N$

(ii) $HCOO^-$

(iii) BrO^-

(a) i < ii < iii

(b) ii < i < iii

(c) Iii < i < ii

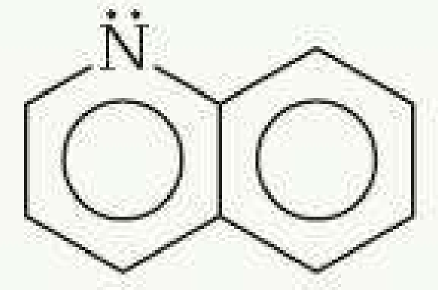
(d) ii < iii < i

(e) iii < ii < i

Practice Exercise 2

(a) Which of the following anions has the largest base-dissociation constant: NO_2^- (K_a of HNO_2 is 4.5 x 10 $^{-4}$), PO_4^{3-} (K_{a1} of H_3PO_4 is 7.5 x 10^{-3}) or N_3^- (K_a of HN_3 is 1.9 x 10^{-5})

(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?

Practice Problem

Calculate the $[OH^-]$ concentration of a 0.10 M NaCN solution. The K_a of HCN is 4.9×10^{-10}.

16.9 Acid-Base Properties of Salt Solutions

Acid–Base Properties of Salts

Many ions react with water to create H^+ or OH^-. The reaction with water is often called **hydrolysis**.

To determine whether a salt is an acid or a base, you need to look at the cation and anion separately.

The cation can be acidic or neutral.

The anion can be acidic, basic, or neutral.

Anions

Anions of strong acids are neutral. For example, Cl^- will *not* react with water, so OH^- can't be formed.

Anions of weak acids are conjugate bases, so they create OH^- in water; e.g., $C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$

Protonated anions from polyprotic acids can be acids or bases: If $K_a > K_b$, the anion will be acidic; if $K_b > K_a$, the anion will be basic.

16.9 Give It Some Thought

Will NO_3^- ions affect the pH of a solution?

What about CO_3^{2-} ions?

Cations

Group I or Group II (Ca^{2+}, Sr^{2+}, or Ba^{2+}) metal cations are neutral.

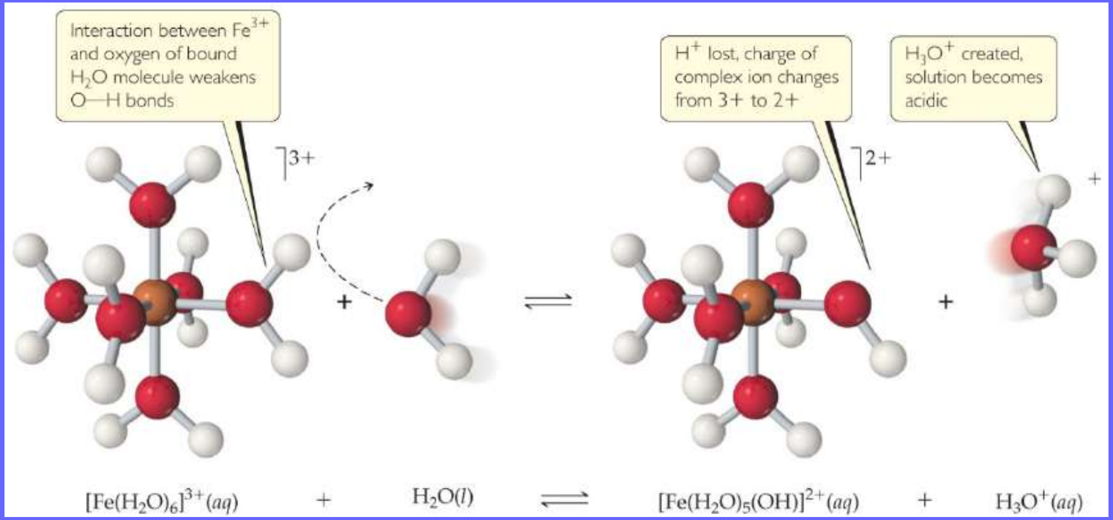
Polyatomic cations are typically the conjugate acids of a weak base; e.g., NH_4^+.

Transition and post-transition metal cations are acidic. Why? (There are no H atoms in these cations!)

Hydrated Cations

Transition and post-transition metals form hydrated cations.

The water attached to the metal is more acidic than free water molecules, making the hydrated ions acidic.



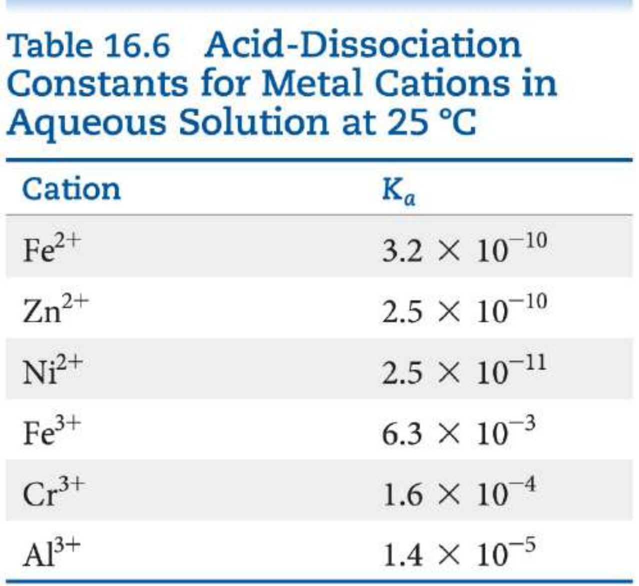


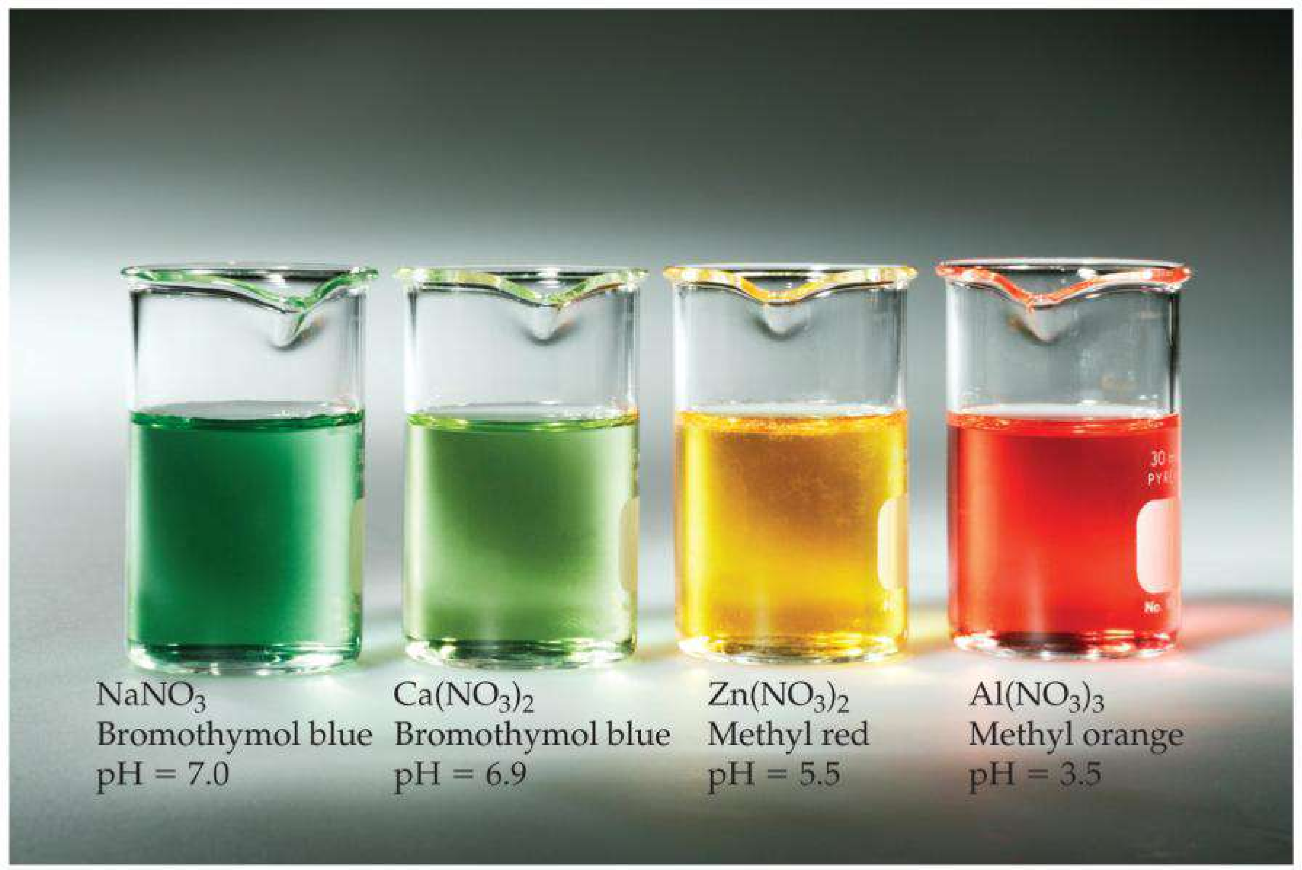
Table 16.6 Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

Cation	K_a
Fe^{2+}	3.2×10^{-10}
Zn^{2+}	2.5×10^{-10}
Ni^{2+}	2.5×10^{-11}
Fe^{3+}	6.3×10^{-3}
Cr^{3+}	1.6×10^{-4}
Al^{3+}	1.4×10^{-5}

Why do we need to use two different acid-base indicators in this figure?

a. The concentration of nitrate affects the indication.

b. The range of pH is too great for one indicator.



Salt Solutions— Acidic, Basic, or Neutral?

1) Group I/II metal cation with anion of a strong acid: neutral
2) Group I/II metal cation with anion of a weak acid: basic (like the anion)
3) Transition/Post-transition metal cation or polyatomic cation with anion of a strong acid: acidic (like the cation)
4) Transition/Post-transition metal cation or polyatomic cation with anion of a weak acid: compare K_a and K_b; whichever is greater dictates what the salt is.

Sample Exercise 16.18

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) $Al(ClO_4)_3$

Practice Exercise 1

Order the following solutions from lowest to highest pH:

(i) 0.10 M NaClO

(ii) 0.10 M KBr

(iii) 0.10 M NH_4ClO_4

(a) i < ii < iii

(b) ii < i < iii

(c) iii < i < ii

(d) ii < iii < i

(e) iii < ii < i

Practice Exercise 2

In each of the following, indicate which salt 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

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.

Practice Exercise 2

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).

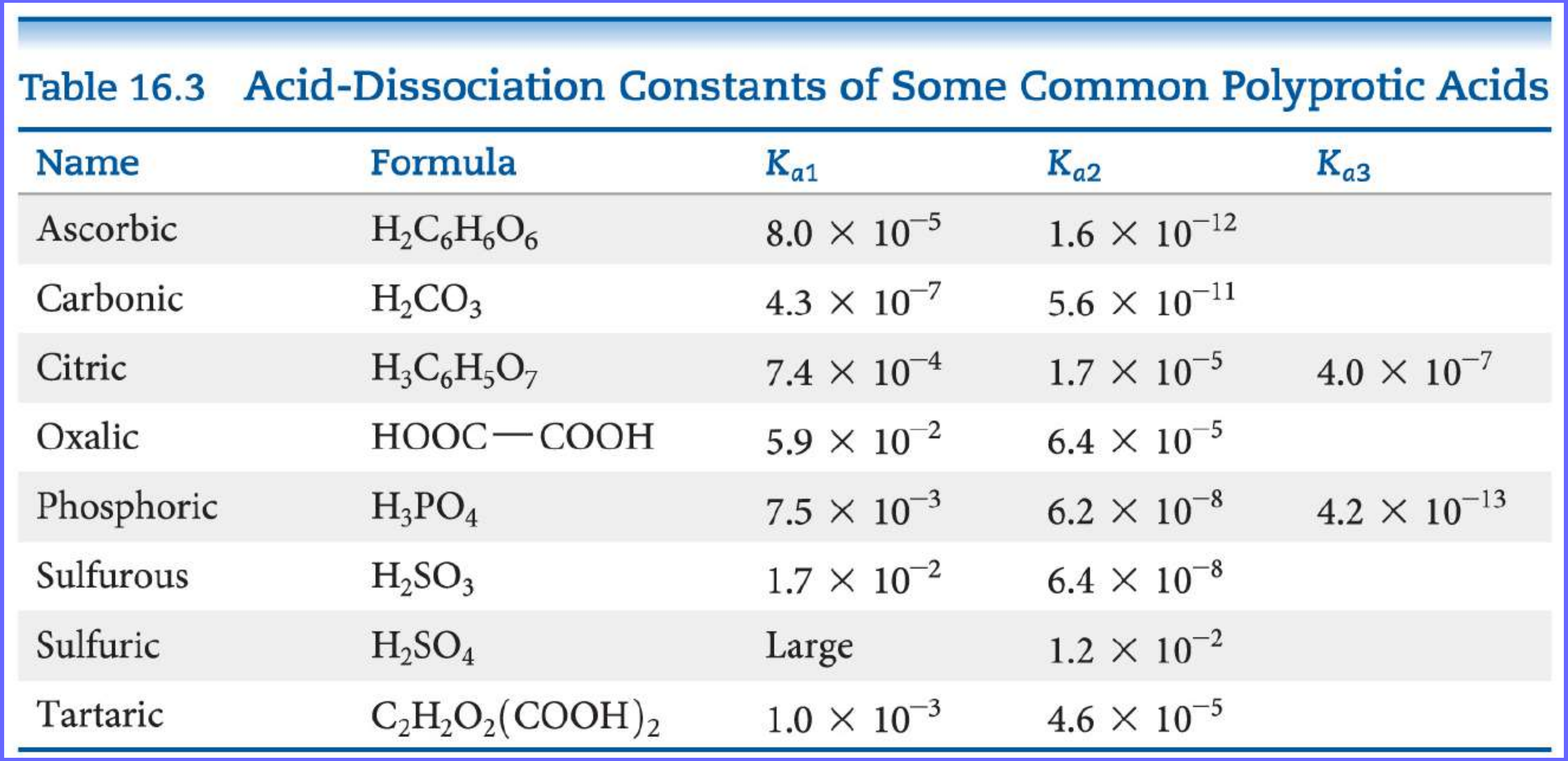


Table 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	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	HOOC—COOH	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$C_2H_2O_2(COOH)_2$	1.0×10^{-3}	4.6×10^{-5}	

16.10 Acid-Base Behavior and Chemical Structure

Factors that Affect Acid Strength

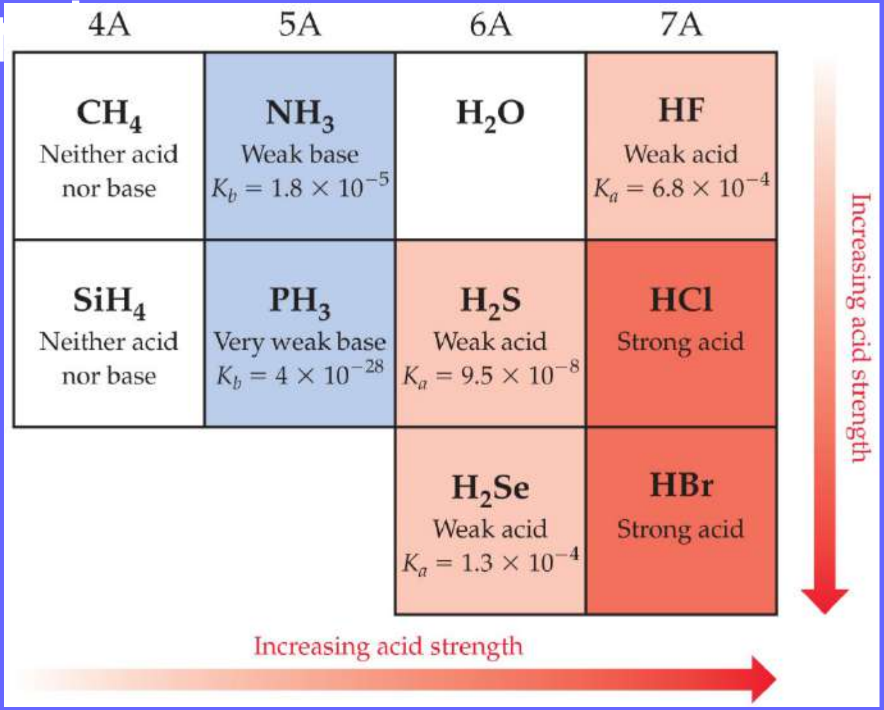
1) H—A bond must be polarized with $\delta+$ on the H atom and $\delta-$ on the A atom
2) Bond strength: Weaker bonds can be broken more easily, making the acid stronger.
3) Stability of A^-: More stable anion means stronger acid.

Binary Acids

Binary acids consist of H and one other element.

Within a group, H—A bo strength is generally the most important factor.

Within a period, bond polarity is the most important factor to determine acid strength.



4A	5A	6A	7A
CH_4 Neither acid nor base	**NH_3** Weak base $K_b = 1.8 \times 10^{-5}$	**H_2O**	**HF** Weak acid $K_a = 6.8 \times 10^{-4}$
SiH_4 Neither acid nor base	**PH_3** Very weak base $K_b = 4 \times 10^{-28}$	**H_2S** Weak acid $K_a = 9.5 \times 10^{-8}$	**HCl** Strong acid
		H_2Se Weak acid $K_a = 1.3 \times 10^{-4}$	**HBr** Strong acid

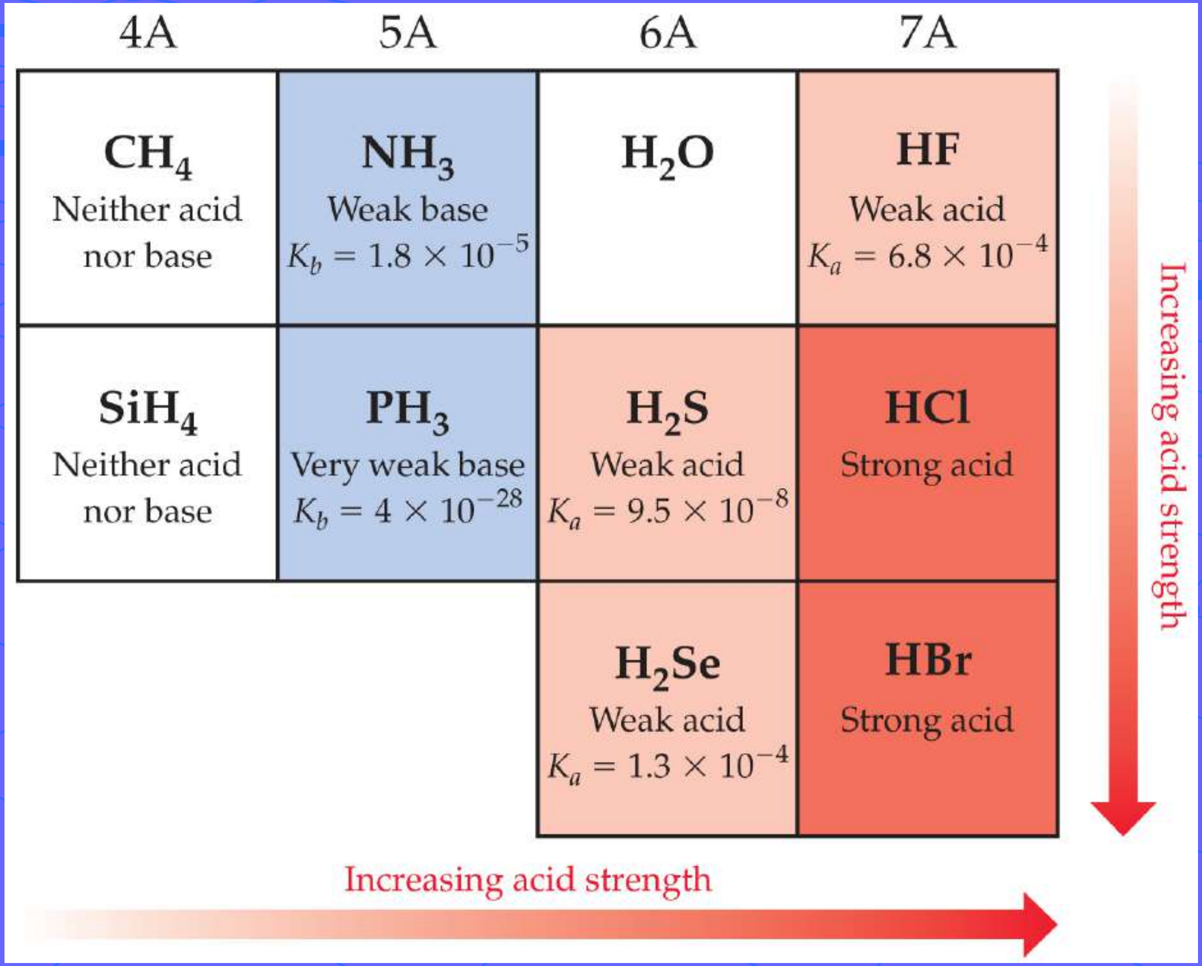
Increasing acid strength

Increasing acid strength

Are the acid properties of HI what you would expect from this figure?

a. Yes, HI is a strong acid.

b. No, HI is a weak acid.



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CH_4 Neither acid nor base	**NH_3** Weak base $K_b = 1.8 \times 10^{-5}$	**H_2O**	**HF** Weak acid $K_a = 6.8 \times 10^{-4}$
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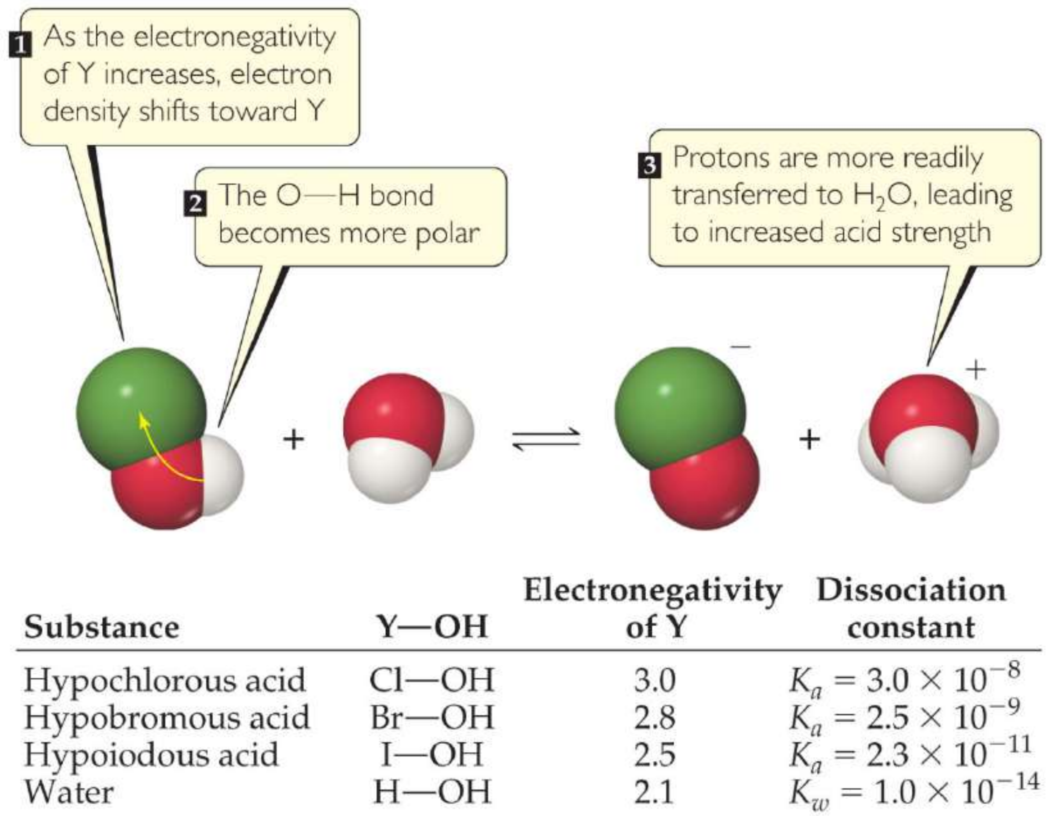
		H_2Se Weak acid $K_a = 1.3 \times 10^{-4}$	**HBr** Strong acid

Oxyacids

- **Oxyacids** consist of H, O, and one other element, which is a nonmetal.
- Generally, as the electronegativity of the nonmetal increases, the acidity increases for acids with the same structure.



1 As the electronegativity of Y increases, electron density shifts toward Y

2 The O—H bond becomes more polar

3 Protons are more readily transferred to H_2O, leading to increased acid strength

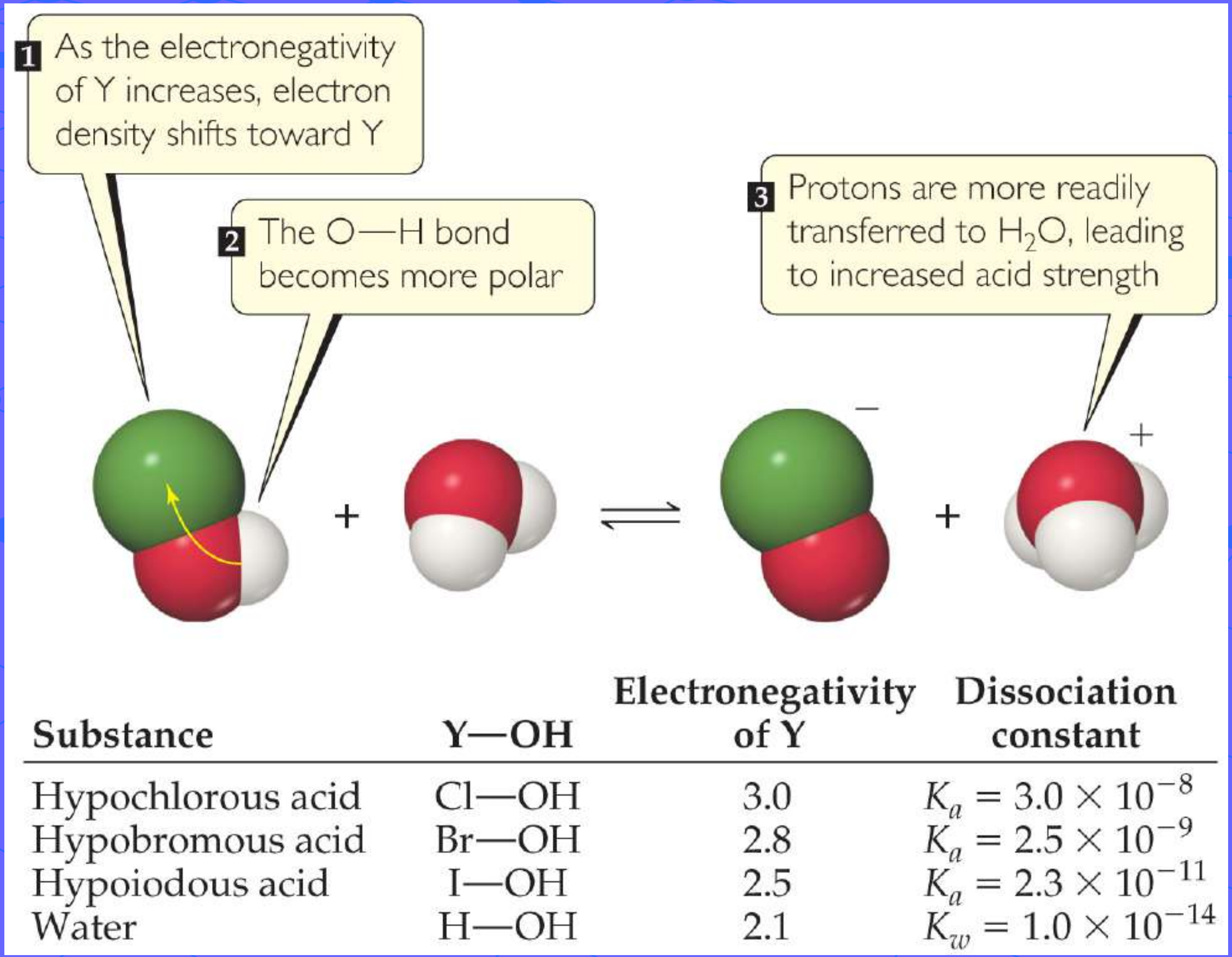
Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

At equilibrium, which of the two species with a halogen atom (green) is present in greater concentration?

a. HOCl

b. OCl^-

c. Cannot tell from information given



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Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
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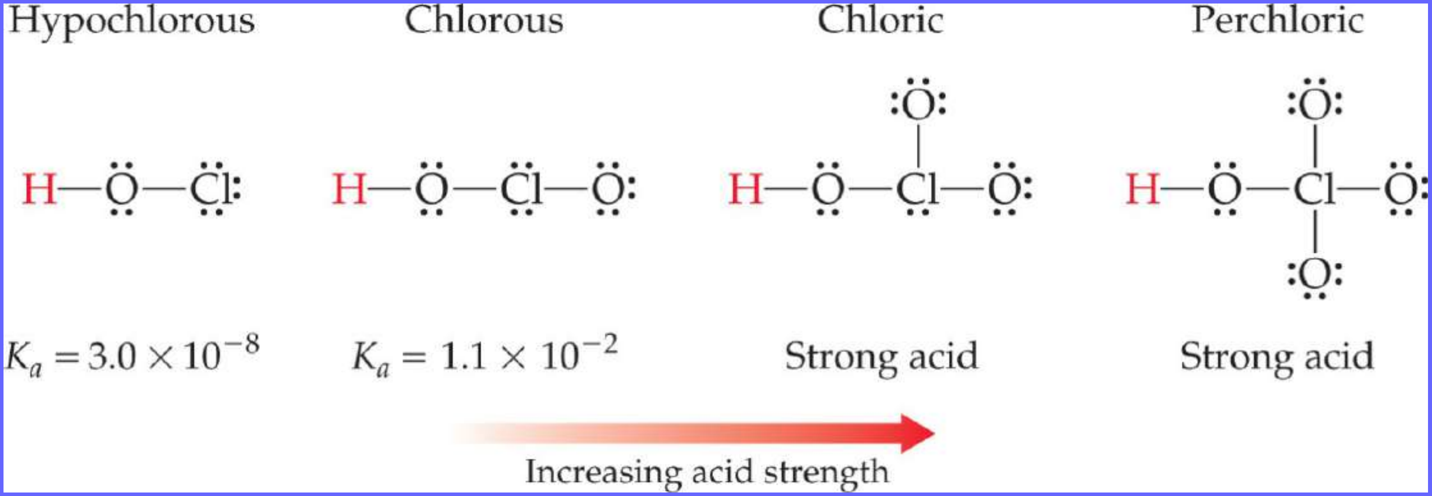
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

Oxyacids with Same "Other" Element

If an element can form more than one oxyacid, the oxyacid with more O atoms is more acidic; e.g., sulfuric acid versus sulfurous acid.

Another way of saying it: If the oxidation number increases, the acidity increases.



16.10 Give It Some Thought

Which acid has the larger acid-dissociation constant, HIO_2 or $HBrO_3$?

Sample Exercise 16.20 Predicting Relative Acidities from Composition and Structure

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

(a) AsH_3, HBr, KH, H_2Se

(b) H_2SO_4, H_2SeO_3, H_2SeO_4.

Practice Exercise 2

In each of the following pairs choose the compound that leads to the more acidic (or less basic) solution:

(a) HBr, HF;

(b) PH_3, H_2S;

(c) HNO_2, HNO_3;

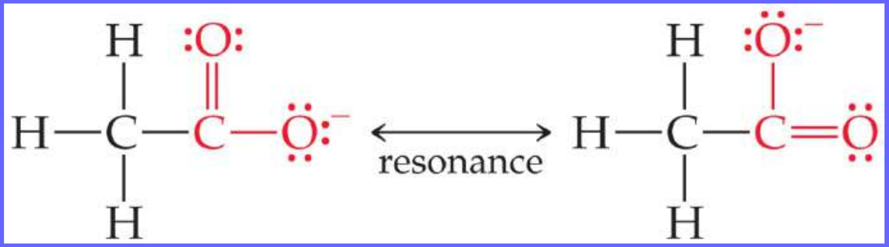
(d) H_2SO_3, H_2SeO_3.

Carboxylic Acids

Carboxylic acids are organic acids containing the —COOH group.

Factors contributing to their acidic behavior:

- Other O attached to C draws electron density from O—H bond, increasing polarity.
- Its conjugate base (carboxylate anion) has resonance forms to stabilize the anion.

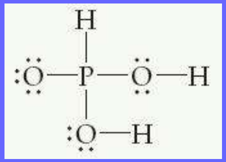


16.10 Give It Some Thought

What group of atoms is present in all carboxylic acids?

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.