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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.

16.1

Acids and Bases: A Brief Review

Arrhenius Definition

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

$$HCl_{(g)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

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

$$NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

16.2

Brønsted-Lowry Acids and Bases

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 H^+ ions from one substance to another.

Brønsted-Lowry

An acid is a proton donor.
A base is a proton acceptor.

$$\mathrm{HCl}(g) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$

When a proton is transferred from HCl to H_2O, HCl acts as the Brønsted-Lowry acid and H_2O acts as the Brønsted-Lowry base.

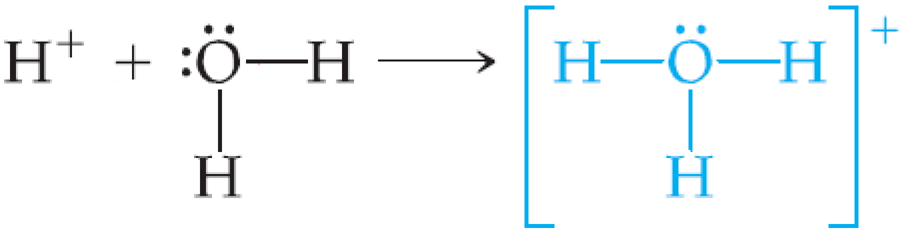
What happens when an acid dissolves in water?
Water acts as a Brønsted-Lowry base and abstracts a proton (H^+) from the acid. As a result, the conjugate base of the acid and a hydronium ion are formed.

An **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

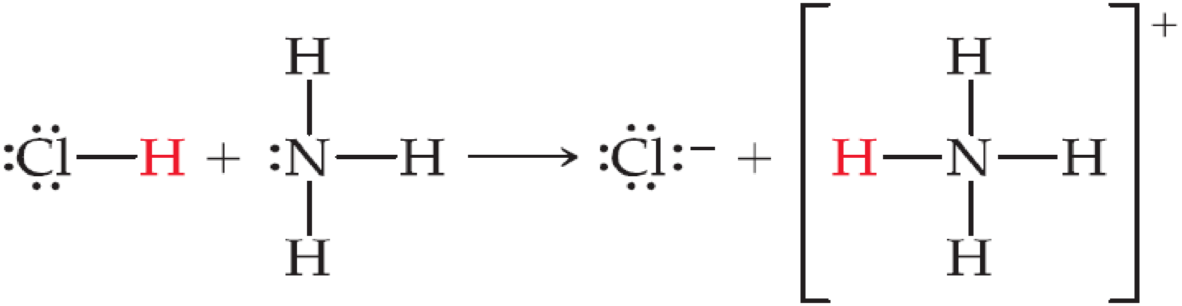
A Brønsted-Lowry base…
…must have a pair of nonbonding electrons

Water molecules to form hydrated hydrogen ions. For example, the interaction of a proton with one water molecule forms the hydronium ion, $H_3O^+(aq)$



Chemists use $H^+(aq)$ and $H_3O^+(aq)$ 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 HCl and NH_3, for example, a proton is transferred from the acid HCl to the base NH_3.



Lets consider another example that compares the relationship between the Arrhenius definition and the Brønsted-Lowry definitions of acids and bases – an aqueous solution of ammonia, in which the following equilibrium occurs:

Ammonia is an Arrhenius base because adding it to water leads to an increase in the concentration of OH^-(aq). It is a Brønsted-Lowry base because it accepts a proton from H_2O. The H_2O molecule in the equation acts as a Brønsted-Lowry acid because it donates a proton to the NH_3 molecule.

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

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 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 H^+ ion.

Some substances can act as an acid in one reaction and as a base in another. For example, H_2O is a Brønsted-Lowry base in its reaction with HCl and a Brønsted-Lowry acid in its reaction with 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., HCO_3^-, HSO_4^-, H_2O

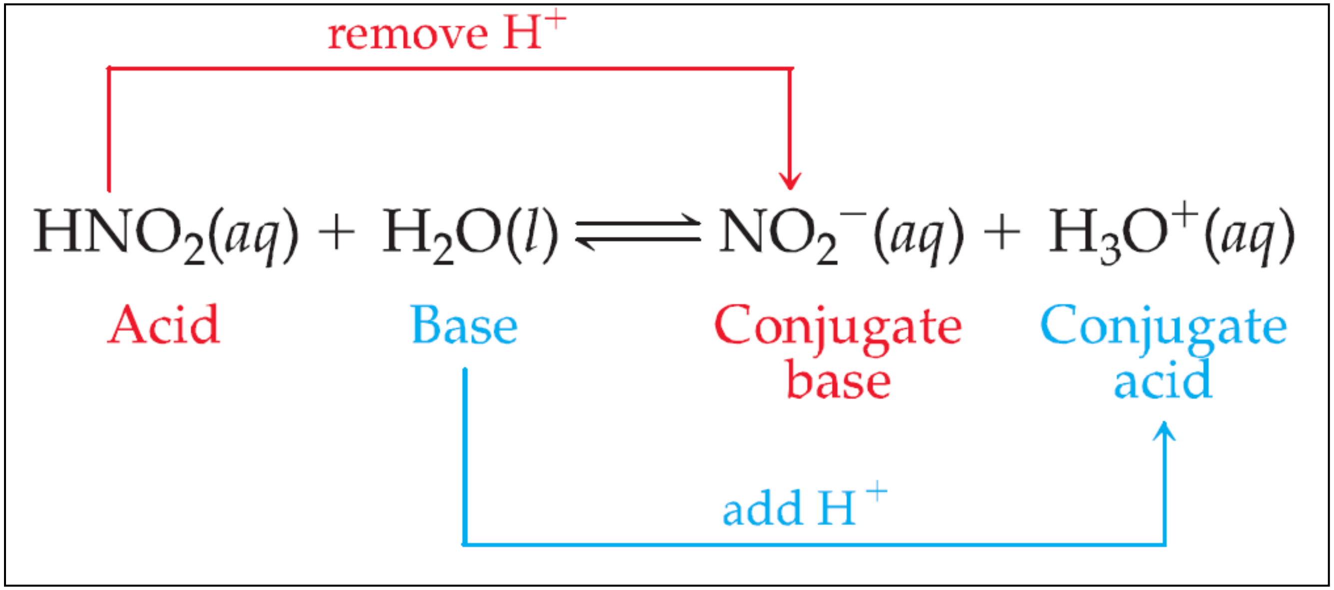
Conjugate Acids and Bases

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

In the forward reaction HX donates a proton to H_2O. Therefore, HX is the Brønsted-Lowry acid, and H_2O is the Brønsted-Lowry base. In the reverse reaction the H_3O^+ ion donates a proton to the X^- ion, so H_3O^+ is the acid and X^- is the base. When the acid HX donates a proton, it leaves X^- which can act as a base. Likewise, when H_2O acts as a base, it generates H_3O^+, which can act as an acid.

An acid and a base such as HX and X^- 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^- is the conjugate base of H_2O, and X^- is the conjugate base of HX. Similarly, every base has associated with it a conjugate acid, formed by adding a proton to the base. Thus, H_3O^+ is the conjugate acid of H_2O, and HX is the conjugate acid of X^-.

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



remove H^+

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

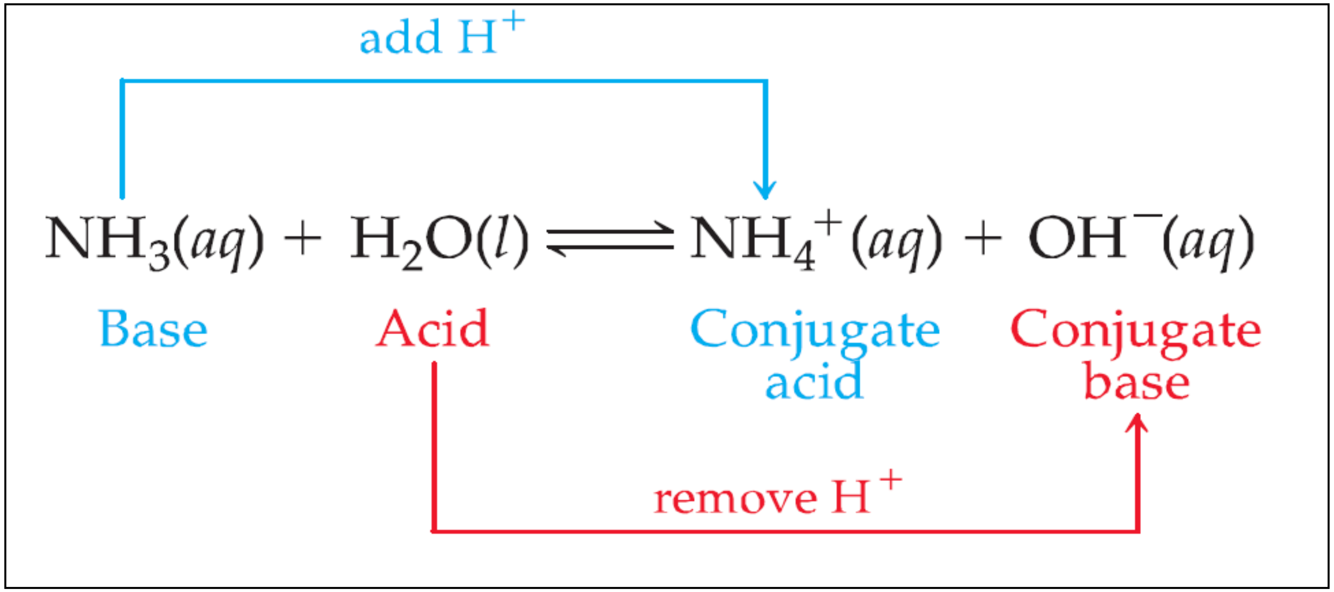
Acid

Base

Conjugate base

Conjugate acid

add H^+



add H^+

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

Base

Acid

Conjugate acid

Conjugate base

remove H^+

Sample Exercise 16.1 Identifying Conjugate Acids and Bases

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

Solution

(a) $HClO_4$ less one proton (H^+) is ClO_4^-. The other conjugate bases are HS^-, PH_3, and CO_3^{2-}.
(b) CN^- plus one proton (H^+) is HCN. The other conjugate acids are HSO_4^-, H_3O^+, and H_2CO_3.
Notice that the hydrogen carbonate ion (HCO_3^-) is amphiprotic. It can act as either an acid or a base.

Practice Exercise

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

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

Sample Exercise 16.2 Writing Equations for Proton-Transfer Reactions

The hydrogen sulfite ion (HSO_3^-) is amphiprotic. **(a)** Write an equation for the reaction of HSO_3^- with water, in which the ion acts as an acid. **(b)** Write an equation for the reaction of HSO_3^- with water, in which the ion acts as a base. In both cases identify the conjugate acid–base pairs.

Solution

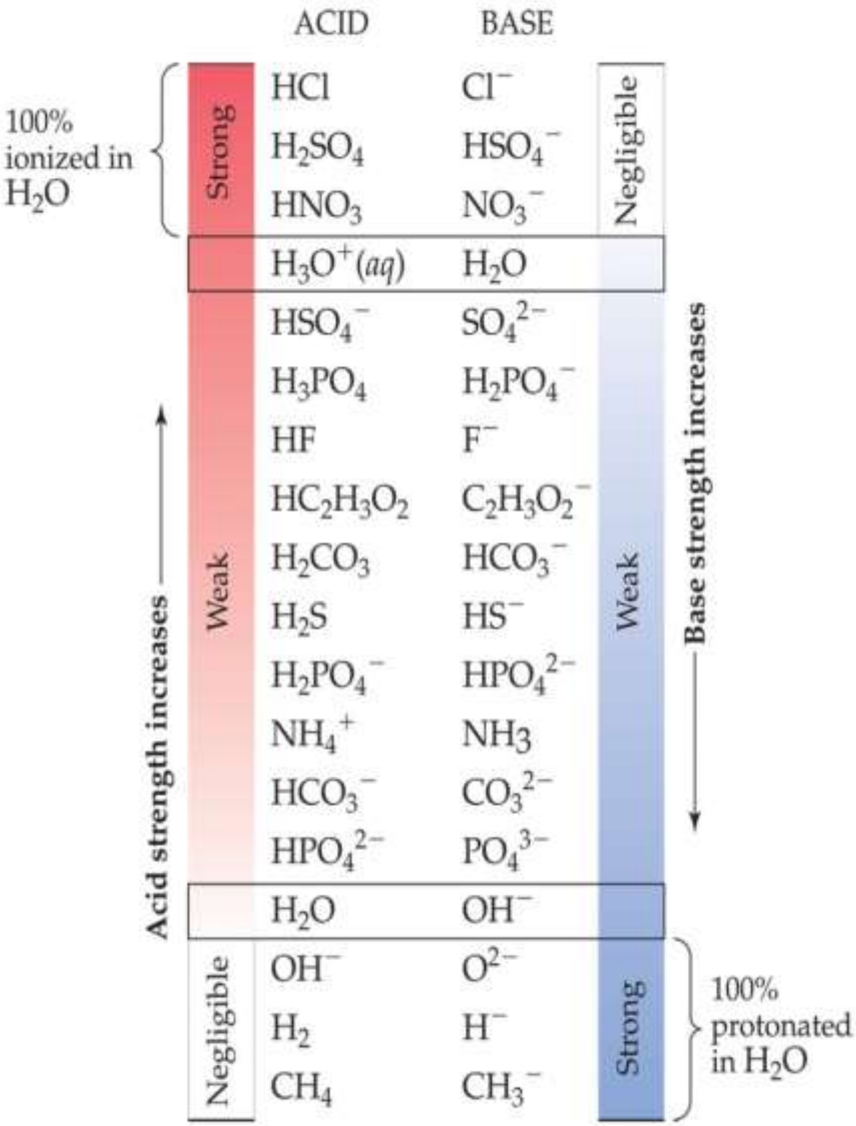
(a) $$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$$

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

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

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

Acid and Base Strength



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

Strong acids are completely dissociated in water.
Their conjugate bases are quite weak.

Weak acids only dissociate partially in water.
Their conjugate bases are weak bases.

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

Example:
CH_4 contains hydrogen but does not demonstrate any acidic behavior in water. Its conjugate base (CH_3^-) is a strong base.

Some acids are better proton donors than others; likewise, some bases are better proton acceptors than others.

The more easily a substance gives up a proton, the less easily its conjugate base accepts a proton. Similarly, the more easily a base accepts a proton, the less easily its conjugate acid gives up a proton.

In other words, 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.

$$\mathrm{HCl}(g) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$

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

$$\mathrm{CH_3COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3COO^-}(aq)$$

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

From these examples, we conclude that in every acid-base reaction the position of the equilibrium favors transfer of the proton from the stronger acid to the stronger base to form the weaker acid and the weaker base. As a result, the equilibrium mixture contains more of the weaker acid and weaker base and less of the stronger acid and stronger base.

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

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

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

Solution

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

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

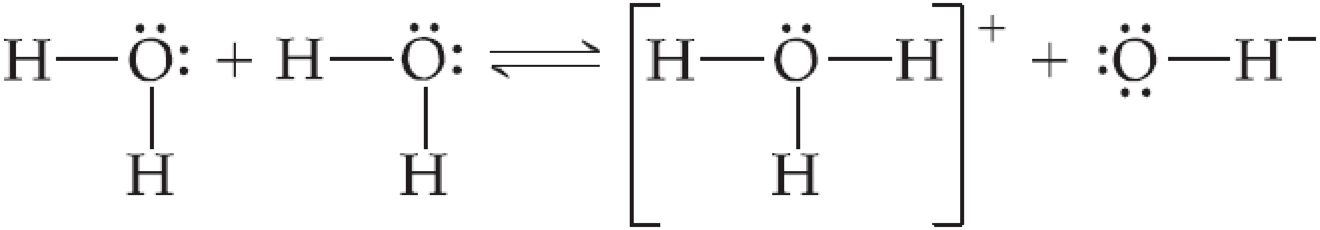
Comment: Of the two acids in the equation, HSO_4^- and HCO_3^-, the stronger one gives up a proton more readily while the weaker one tends to retain its proton. Thus, the equilibrium favors the direction in which the proton moves from the stronger acid and becomes bonded to the stronger base.

16.3

The Autoionization of Water

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.



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

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 H_2O molecules and is an **extremely poor conductor of electricity**. Nevertheless, the autoionization of water is very important.

The Ion-Product Constant of Water

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

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

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.

The term $[H_2O]$ is excluded from the equilibrium-constant expression because we exclude the concentration of pure solids and liquids.

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14} \quad \text{(at 25 °C)}$$

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

Thus, this Equation is taken to be valid for any dilute aqueous solution, and it can be used to calculate either $[H^+]$ (if $[OH^-]$ is known) or $[OH^-]$ (if $[H^+]$ is known).

A solution in which **$[H^+] = [OH^-]$** is said to be **neutral**. In most solutions H^+ and 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 1.0×10^{-14}.

In **acidic** solutions **$[H^+]$ exceeds $[OH^-]$**.
In **basic** solutions **$[OH^-]$ exceeds $[H^+]$**.

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

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

Solution

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

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

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

Practice Exercise

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:
(a) $[H^+] = 4 \times 10^{-9}\,M$; **(b)** $[OH^-] = 1 \times 10^{-7}\,M$; **(c)** $[OH^-] = 7 \times 10^{-13}\,M$.

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

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

Calculate the concentration of $H^+(aq)$ in **(a)** a solution in which $[OH^-]$ is 0.010 *M*, **(b)** a solution in which $[OH^-]$ is 1.8×10^{-9} *M*.
Note: In this problem and all that follow, we assume, unless stated otherwise, that the temperature is 25 ºC.

Solution

(a) Using Equation, 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

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

16.4

The pH Scale

pH

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

$$\mathbf{pH = -\log [H_3O^+] \quad or \quad pH = -\log [H^+]}$$

- In pure water,

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

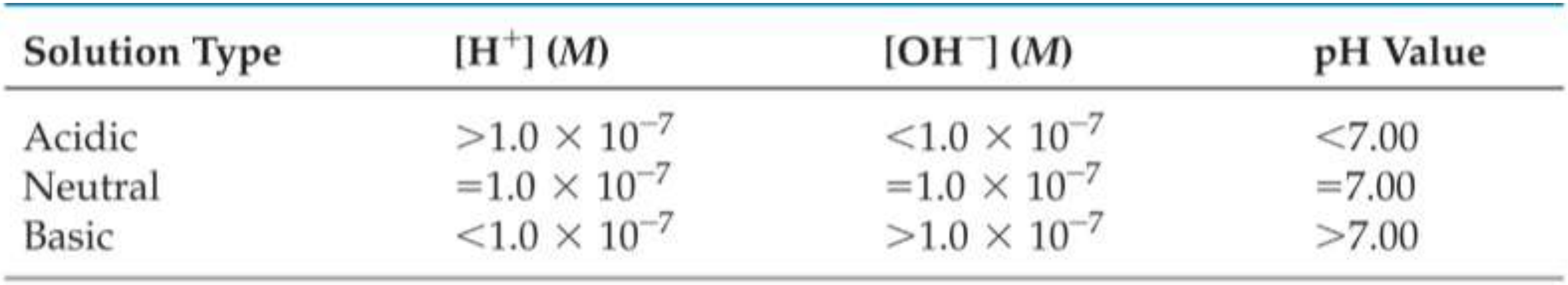
- Since in pure water **$[H_3O^+] = [OH^-]$**,

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

- Therefore, in pure water,

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

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



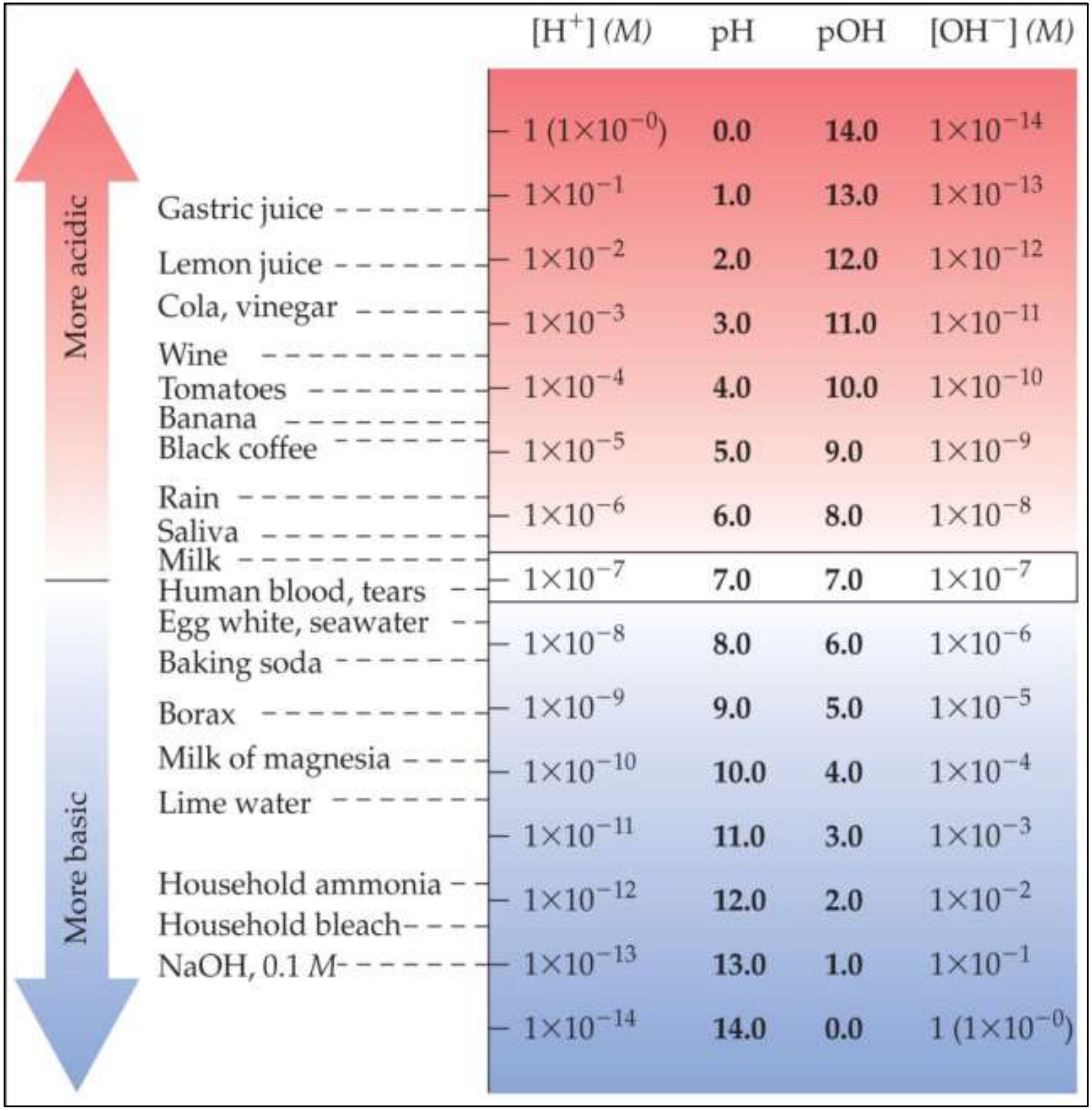
Solution Type	$[H^+]$ (M)	$[OH^-]$ (M)	pH Value
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	$=7.00$
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

What happens to the pH of a solution as we make the solution acidic? An acidic solution is one in which $[H^+] > 1.0 \times 10^{-7}$ M. because of the negative sign in Equation ($pH = -\log[H^+]$), the pH decreases as $[H^+]$ increases.

Examples …

$[H^+] = 1.0 \times 10^{-3}$ M calculate pH
$pH = -\log(1.0 \times 10^{-3}) = -(-3.00) = 3$

A sample of freshly pressed apple juice has a pH of 3.76. calculate $[H^+]$
$pH = -\log[H^+] = 3.76$
$\text{Log}[H^+] = -3.76$
$[H^+] = \text{antilog}(-3.76) = 10^{-3.76} = 1.7 \times 10^{-4}$ M



$[H^+]$ (M)	pH	pOH	$[OH^-]$ (M)
$1\ (1 \times 10^{-0})$	**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**	$1\ (1 \times 10^{-0})$

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.

In **biological systems** many reactions involve proton transfers and have rates that depend on [H^+]. Because the speeds of these reactions are crucial, the pH of biological fluids must be **maintained within narrow limits**.

For example, human blood has a normal pH range of **7.35 to 7.45**. Illness and even death can result if the pH varies much from this narrow range.

Sample Exercise 16.6 Calculating pH from [H⁺]

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

Solution

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

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

Because $\mathbf{1.0} \times 10^{-12}$ has two significant figures, the pH has two decimal places, 12.**00**.

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

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

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

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

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, we have

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

Thus,

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

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

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

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

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
  - **pOH = -log $[OH^-]$**
  - **pK_w = -log K_w**

px = -logx

Larger the x, smaller the px

Because

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

we know that

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

or, in other words,

$$pH + pOH = pK_w = 14.00$$

Measuring pH

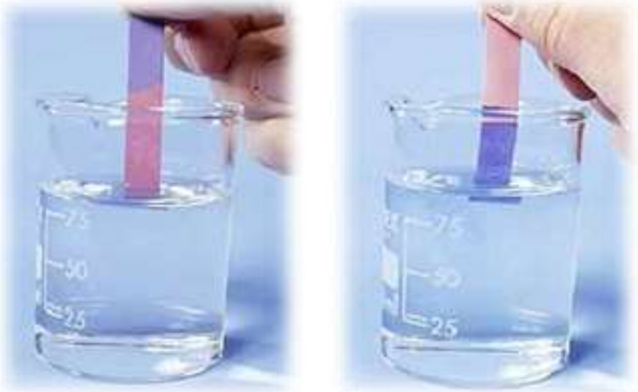
For accurate measurements, one uses a **pH meter**, which measures the **voltage** in the solution.

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 ~pH = 8
- “Blue” paper turns red below ~pH = 5

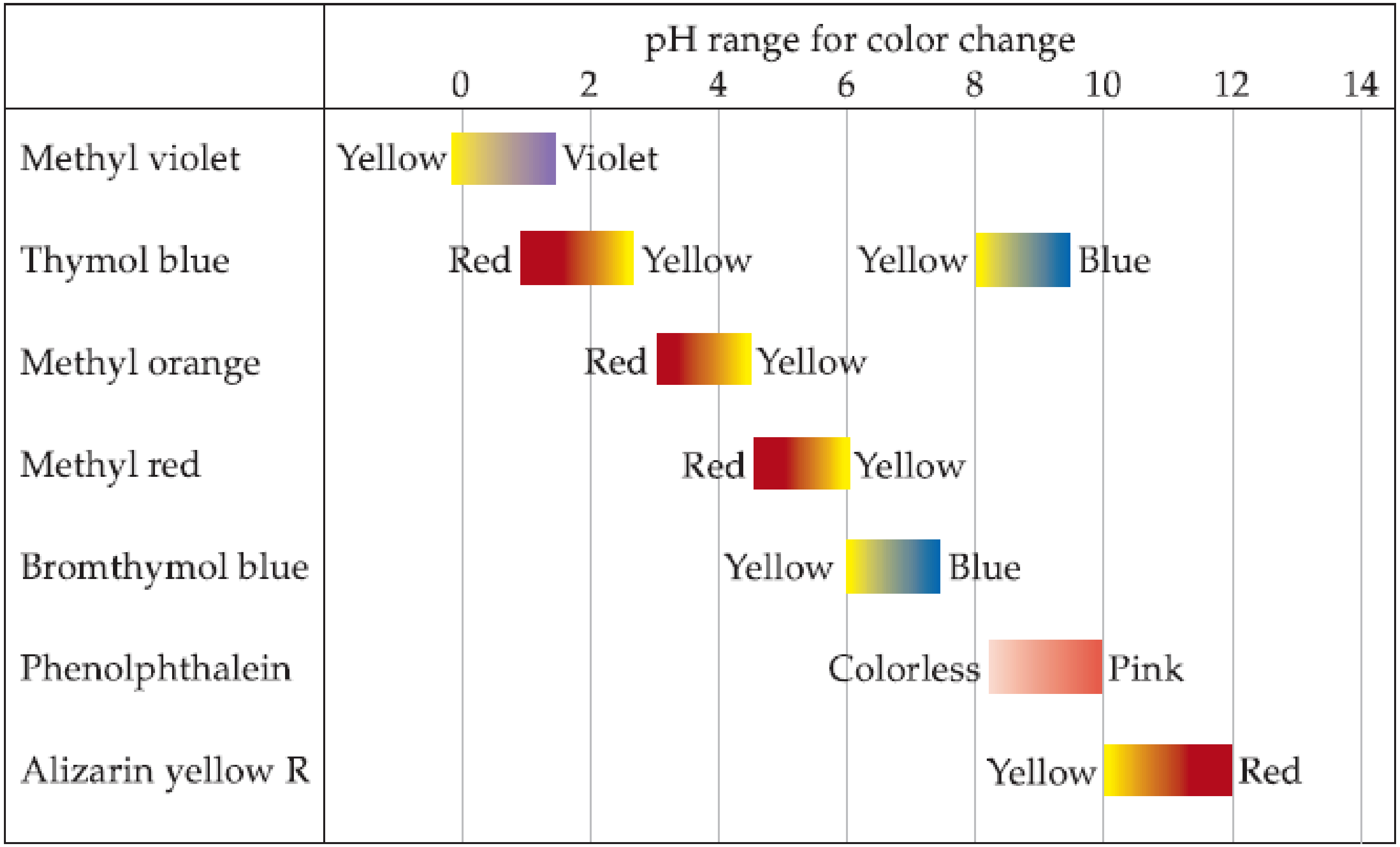
– Universal indicator papers

Papers impregnated with several indicators.

We manufacture a variety of pH Indicator papers covering the widest possible range of application in education, science, medicine and industry.

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



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.

16.5

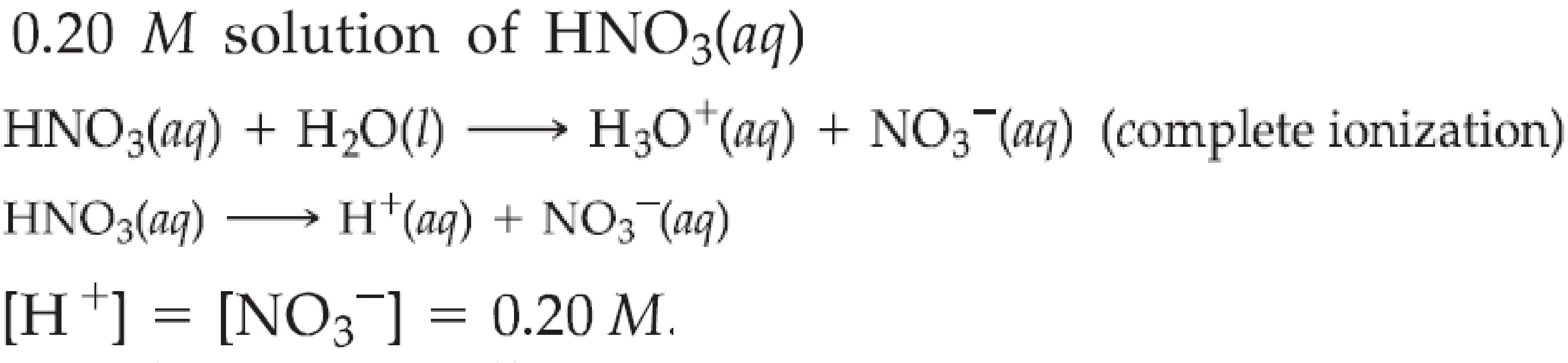
Strong Acids and Bases

- The seven most common **strong acids** are HCl, HBr, HI, HNO_3, $HClO_3$, and $HClO_4$ (monoprotic) and H_2SO_4 (diprotic).
- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.
- For the monoprotic strong acids,

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

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

For example,



0.20 *M* solution of $HNO_3(aq)$

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq) \quad \text{(complete ionization)}$$

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

$$[H^+] = [NO_3^-] = 0.20\ M.$$

Sample Exercise 16.8 Calculating the pH of a Strong Acid

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

Solution

The pH of the solution is given by

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

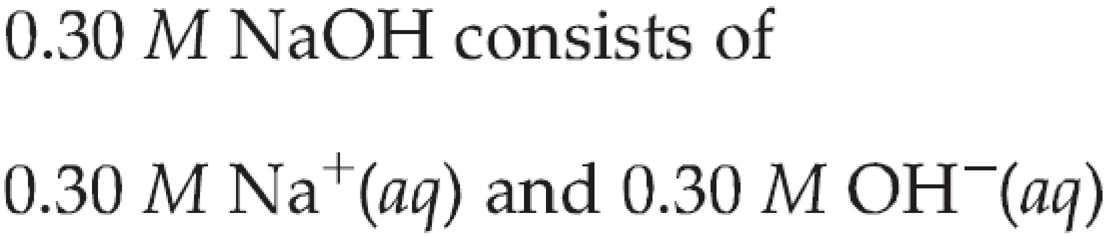
Check: Because $[H^+]$ lies between 1×10^{-2} and 1×10^{-1}, the pH will be between 2.0 and 1.0. Our calculated pH falls within the estimated range. Furthermore, because the concentration has two significant figures, the pH has two decimal places.

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

- Again, these substances dissociate completely in aqueous solution.

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

For example,



0.30 *M* NaOH consists of

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

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 $Ca(OH)_2$?

Solution

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

Method 1:

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

Method 2:

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

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

Method 1:

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

Method 2:

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

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. $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$, 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 Na_2O and CaO, are often used in industry when a strong base is needed. The O^{2-} reacts with water to form OH^-, leaving virtually no O^{2-} remaining in the solution:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2\,OH^-(aq)$$

Thus, a solution formed by dissolving 0.010 mol of $Na_2O(s)$ in enough water to form 1.0 L of solution will have $[OH^-] = 0.020$ M and a pH of 12.30.

16.6

Weak Acids

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,

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

or

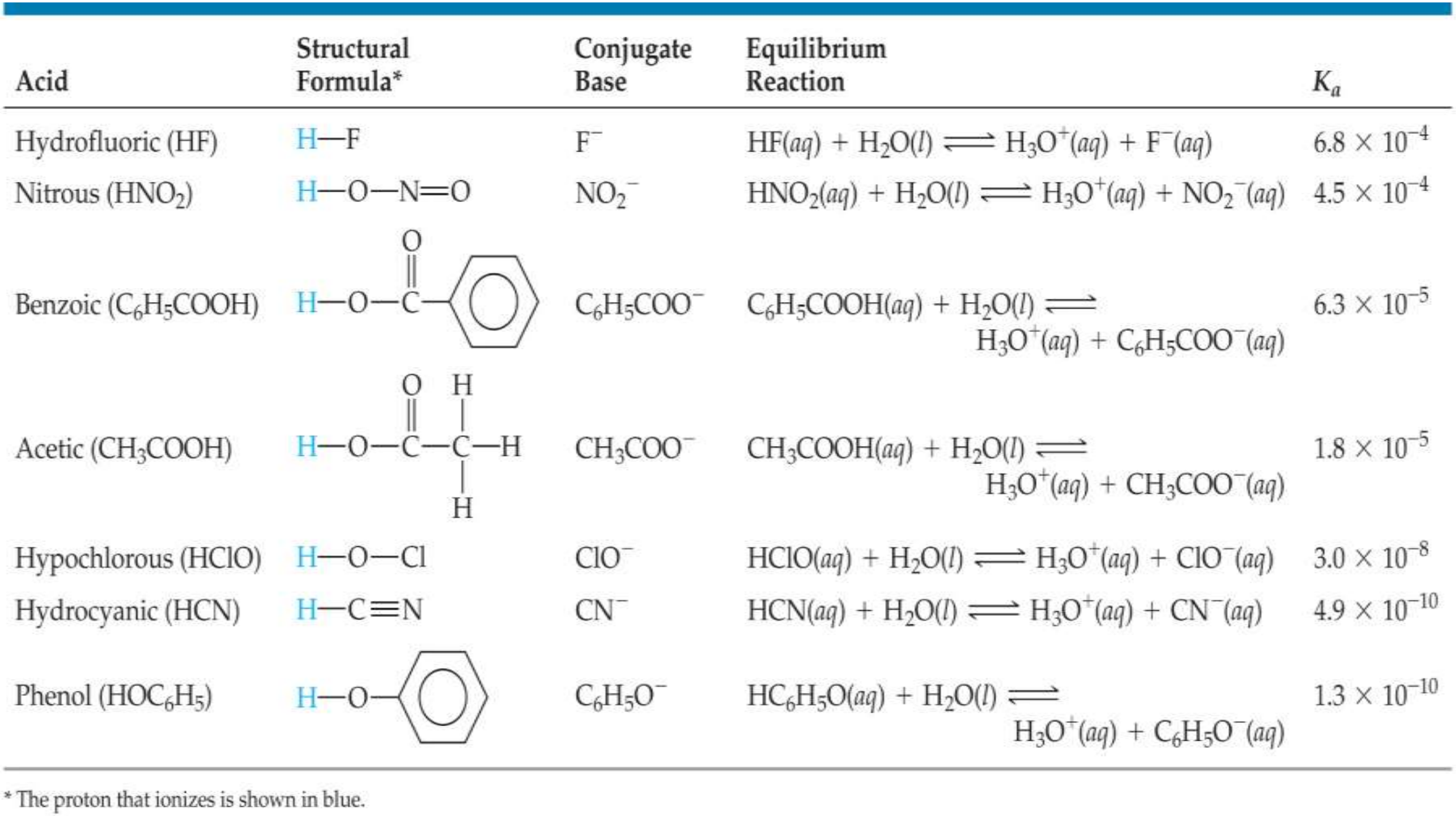
$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Either of the following ways, depending on whether the hydrated proton is represented as $H_3O^+(aq)$ or $H^+(aq)$:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

This equilibrium constant K_a is called the **acid-dissociation constant**. Because H_2O 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 (HOC_6H_5) is the weakest.



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

* The proton that ionizes is shown in blue.

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.

Calculating K_a from the pH

In order to calculate either the K_a value for a weak acid or the pH of its solutions, we will use many of the skills for solving equilibrium problems.

In many cases the small magnitude of K_a allows us to use approximations to simplify the problem.

In doing these calculations, it is important to realize that proton-transfer reactions are generally very rapid. As a result, the measured or calculated pH for a weak acid always represents an equilibrium condition.

Sample Exercise 16.10 Calculating K_a from Measured pH

A student prepared a 0.10 *M* solution of formic acid (HCOOH) and measured its pH. The pH at 25 ºC was found to be 2.38. Calculate K_a for formic acid at this temperature.

Solution

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

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

The equilibrium-constant expression is

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

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

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

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

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

We can do a little accounting to determine the concentrations of the species involved in the equilibrium.

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

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

Notice that we have neglected the very small concentration of $H^+(aq)$ that is due to the autoionization of H_2O. Notice also that the amount of HCOOH that ionizes is very small compared with the initial concentration of the acid. To the number of significant figures we are using, the subtraction yields 0.10 *M*:

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

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

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

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 $H^+(aq)$ that forms, assuming that the autoionization of water is negligible.

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

For example, a 0.035 M solution of HNO_2 contains 3.7×10^{-3} M $H^+(aq)$. Thus, the percent ionization is

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HNO_2]_{\text{initial}}} \times 100\% = \frac{3.7 \times 10^{-3}\ M}{0.035\ M} \times 100\% = 11\%$$

Sample Exercise 16.11 Calculating Percent Ionization

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

Solution

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

Calculating pH from K_a

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

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

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

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

	$CH_3COOH(aq)$ ⇌	$H^+(aq)$ +	$CH_3COO^-(aq)$
Initial	$0.30\ M$	0	0
Change	$-x\ M$	$+x\ M$	$+x\ M$
Equilibrium	$(0.30 - x)\ M$	$x\ M$	$x\ M$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5}$$

$$0.30 - x \simeq 0.30$$

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

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

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

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

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

Percent ionization of CH_3COOH =

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

Sample Exercise 16.12 Using K_a to Calculate pH

Calculate the pH of a 0.20 *M* solution of HCN ($K_a = 9.9 \times 10^{-6}$).

Solution

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

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

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

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

	$HCN(aq)$ ⇌	$H^+(aq)$ +	$CN^-(aq)$
Initial	$0.20\ M$	0	0
Change	$-x\ M$	$+x\ M$	$+x\ M$
Equilibrium	$(0.20 - x)\ M$	$x\ M$	$x\ M$

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

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

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

$$0.20 - x \simeq 0.20$$

Thus,

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

Solving for *x*, we have

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

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

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

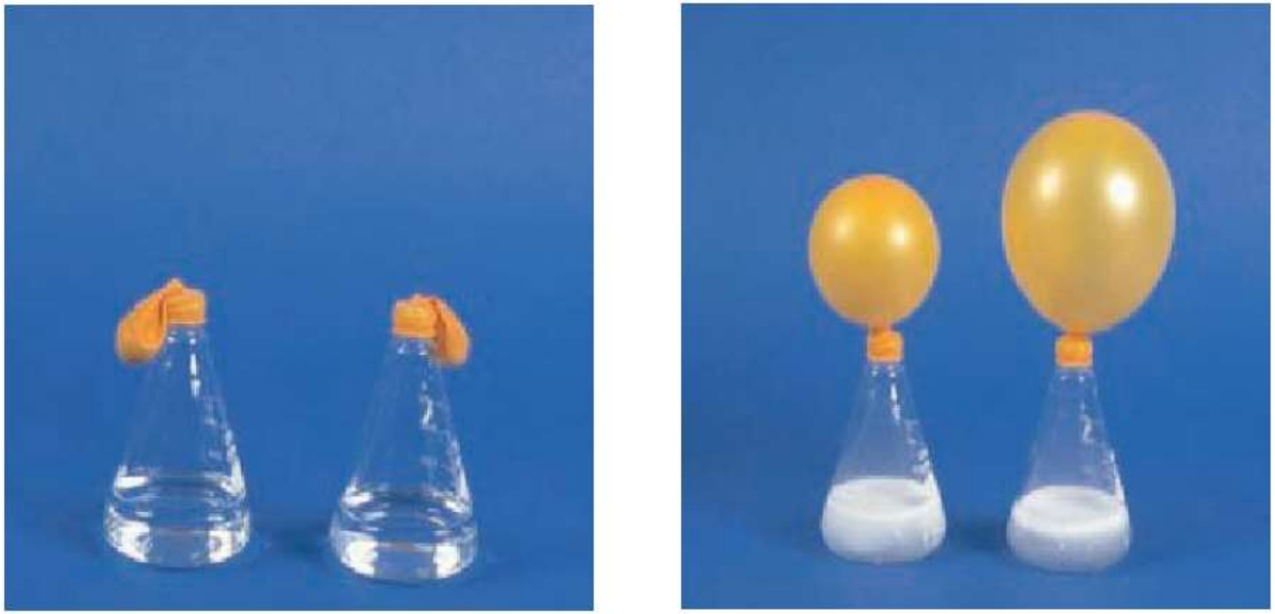
$$pH = -\log[H^+] = -\log(9.9 \times 10^{-6}) = 5.00$$

The properties of the acid solution that relate directly to the concentration of H^+(aq), such as electrical conductivity and rate of reaction with an active metal, are much less evident for a solution of weak acid than for a solution of a strong acid of the same concentration.

The Figures compare the behavior of 1 M CH_3COOH and 1 M HCl. The 1 M CH_3COOH contains only 0.004 M H^+(aq), whereas the 1 M HCl solution contains 1 M H^+(aq). As a result, the rate of reaction is much faster for the solution of HCl.

(a) the flask on the left contains 1 M CH_3COOH, the one on the right contains 1 M HCl with the same amount of magnesium metal.

(b) when the Mg is dropped into the acid, H_2 gas is formed. The rate of H_2 formation is higher for HCl on the right. Eventually, the same amount of H_2 forms in both cases.

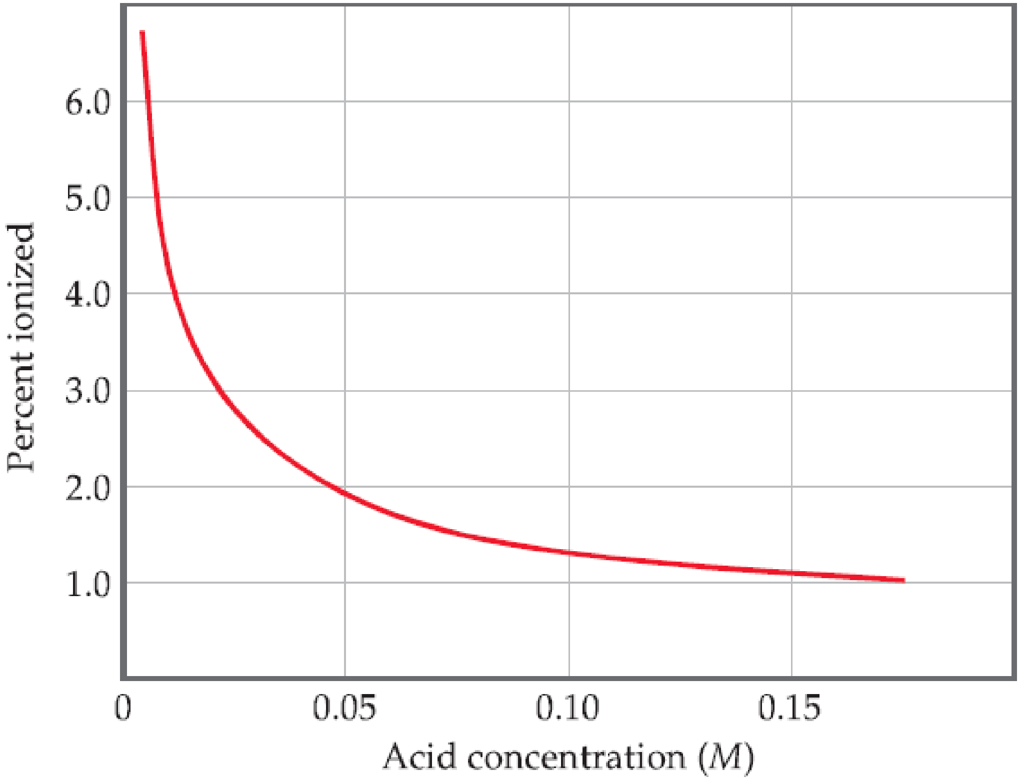


(a)

(b)

As the concentration of a weak acid increases, **the equilibrium concentration of $H^+(aq)$ increases**, as expected. However, **the percent ionization decreases as the concentration increases**. Thus, the concentration of $H^+(aq)$ is not directly proportional to the concentration of the weak acid.

For example, doubling the concentration of a weak acid does not double the concentration of $H^+(aq)$.



The effect of concentration on ionization of a weak acid. The percent ionization of a weak acid decreases with increasing concentration. The data shown are for acetic acid.

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) The equilibrium reaction and equilibrium concentrations are as follows:

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

The equilibrium-constant expression is

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

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

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

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

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

This equation can be solved using the standard quadratic formula. Substituting the appropriate numbers gives

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

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

Of the two solutions, only the one that gives a positive value for x is chemically reasonable. Thus, From our result, we can calculate the percent of molecules ionized:

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

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

(b) Proceeding similarly for the 0.010 *M* solution, we have Solving the resultant quadratic expression, we obtain

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

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

The percentage of molecules ionized is

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

Polyprotic Acids

Polyprotic acids have more than one ionizable H atom

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.7 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-8}$$

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

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

Because of electrostatic attractions, we would expect a positively charged proton to be lost more readily from the neutral H_2SO_3 molecule than from the negatively charged HSO_3^- ion. This observation is general: **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 $\boldsymbol{K_a}$ values become successively smaller as successive protons are removed.

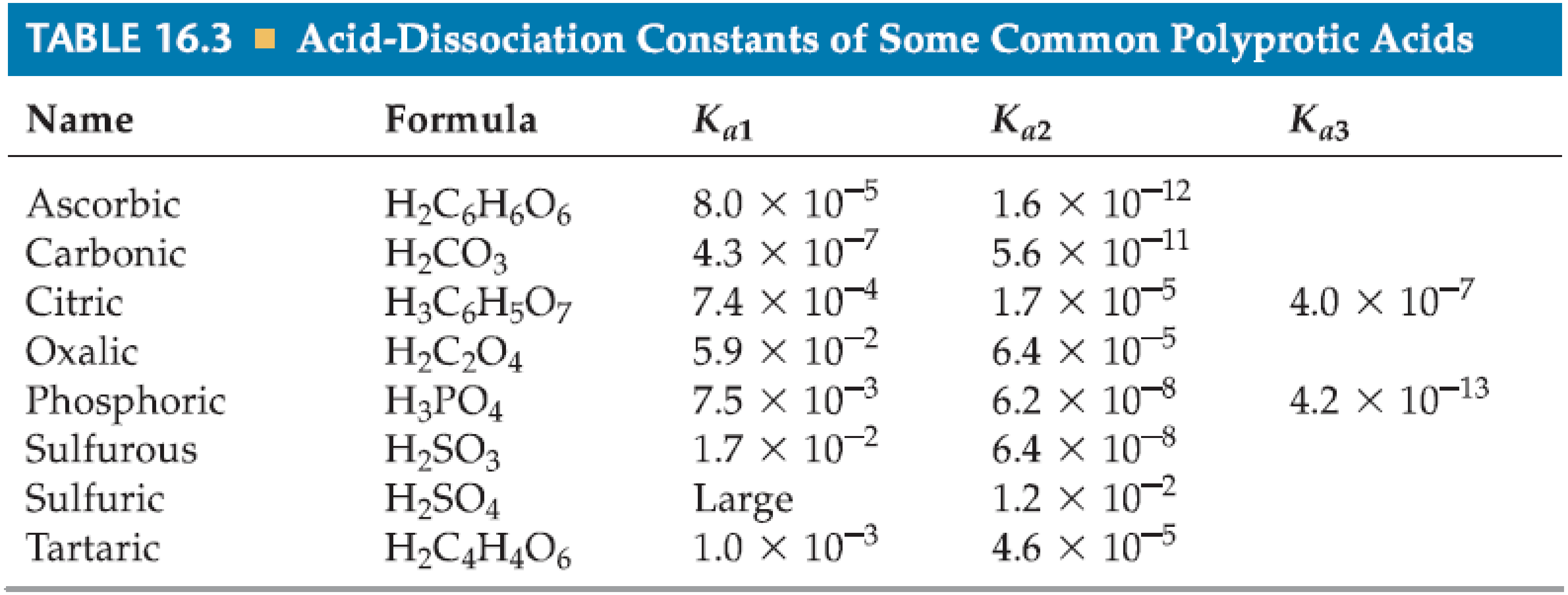


TABLE 16.3 ■ Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	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	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

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:

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \quad \text{(complete ionization)}$$

HSO_4^-, on the other hand, is a weak acid for which $\boldsymbol{K_{a2}} = 1.2 \times 10^{-2}$.

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

Solution

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

	$H_2CO_3(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$HCO_3^-(aq)$
Initial	$0.0037\ M$	0	0
Change	$-x\ M$	$+x\ M$	$+x\ M$
Equilibrium	$(0.0037 - x)\ M$	$x\ M$	$x\ M$

The equilibrium-constant expression is as follows:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.0037 - x} = 4.3 \times 10^{-7}$$

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

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

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

$$0.0037 - x \simeq 0.0037$$

Thus,

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

Solving for x, we have

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

$$x = [H^+] = [HCO_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\ M$$

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

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

Comment: If we were asked to solve for $[CO_3^{2-}]$, we would need to use K_{a2}. Let's illustrate that calculation. Using the values of $[HCO_3^-]$ and $[H^+]$ calculated above, and setting $[CO_3^{2-}] = y$, we have the following initial and equilibrium concentration values:

	$HCO_3^-(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$CO_3^{2-}(aq)$
Initial	$4.0 \times 10^{-5}\ M$	$4.0 \times 10^{-5}\ M$	0
Change	$-y\ M$	$+y\ M$	$+y\ M$
Equilibrium	$(4.0 \times 10^{-5} - y)\ M$	$(4.0 \times 10^{-5} + y)\ M$	$y\ M$

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

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11}\ M = [CO_3^{2-}]$$

The value calculated for y is indeed very small compared to 4.0×10^{-5}, showing that our assumption was justified. It also shows that the ionization of HCO^{3-} is negligible compared to that of H_2CO_3, as far as production of H^+ is concerned. However, it is the *only* source of CO_3^{2-}, which has a very low concentration in the solution. Our calculations thus tell us that in a solution of carbon dioxide in water, most of the CO_2 is in the form of CO_2 or H_2CO_3, a small fraction ionizes to form H^+ and HCO^{3-}, and an even smaller fraction ionizes to give CO_3^{2-}. Notice also that $[CO_3^{2-}]$ is numerically equal to K_{a2}.

16.7

Weak Bases

Many substances behave as weak bases in water. Weak bases react with water, abstracting protons from H_2O, thereby forming the conjugate acid of the base and OH^- ions.

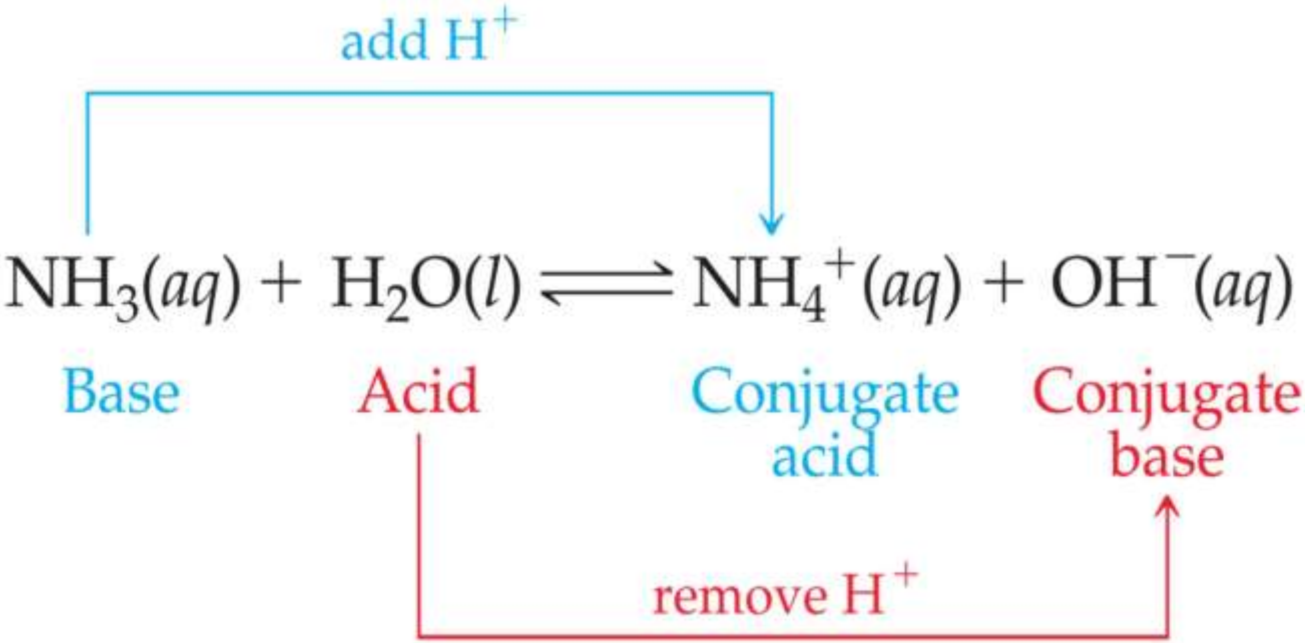
Bases react with water to produce hydroxide ion.

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

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_2O to form the corresponding conjugate acid and OH^-.

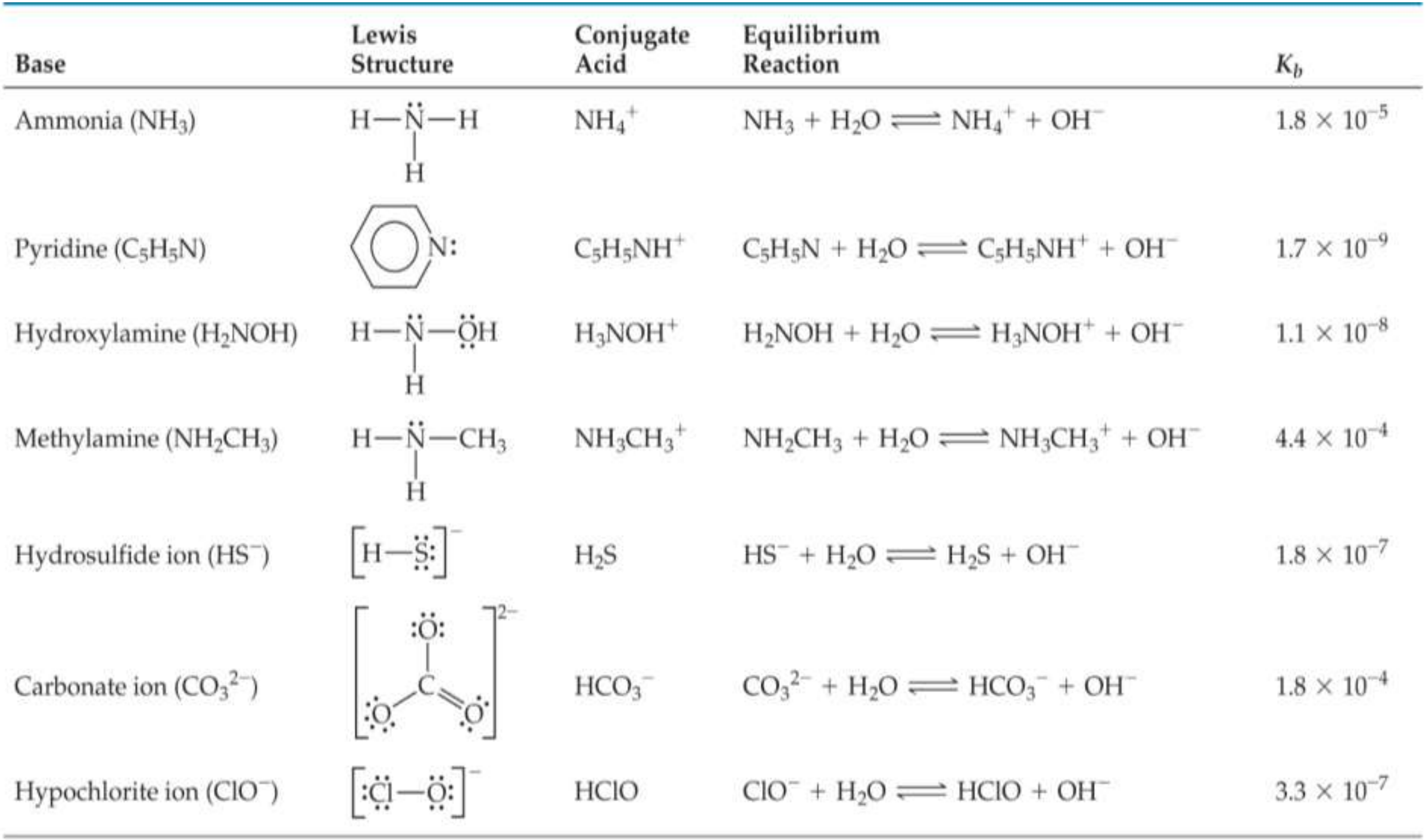


$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The equilibrium constant expression for this reaction is

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

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_3)	H—N̈—H | H	NH_4^+	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C_5H_5N)	N:	$C_5H_5NH^+$	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)	H—N̈—ÖH | H	H_3NOH^+	$H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)	H—N̈—CH_3 | H	$NH_3CH_3^+$	$NH_2CH_3 + H_2O \rightleftharpoons NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$[H—\ddot{S}:]^-$	H_2S	$HS^- + H_2O \rightleftharpoons H_2S + OH^-$	1.8×10^{-7}
Carbonate ion (CO_3^{2-})	$[\,:\ddot{O}:\,]^{2-}$ | C :Ö: Ö:	HCO_3^-	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$[:\ddot{Cl}—\ddot{O}:]^-$	$HClO$	$ClO^- + H_2O \rightleftharpoons HClO + OH^-$	3.3×10^{-7}

These bases contain one or more lone pairs of electrons because a lone pair is necessary to form the bond with H^+. 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 OH^-

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

Solution

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

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

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

We then tabulate the equilibrium concentrations involved in the equilibrium:

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

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

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

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

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

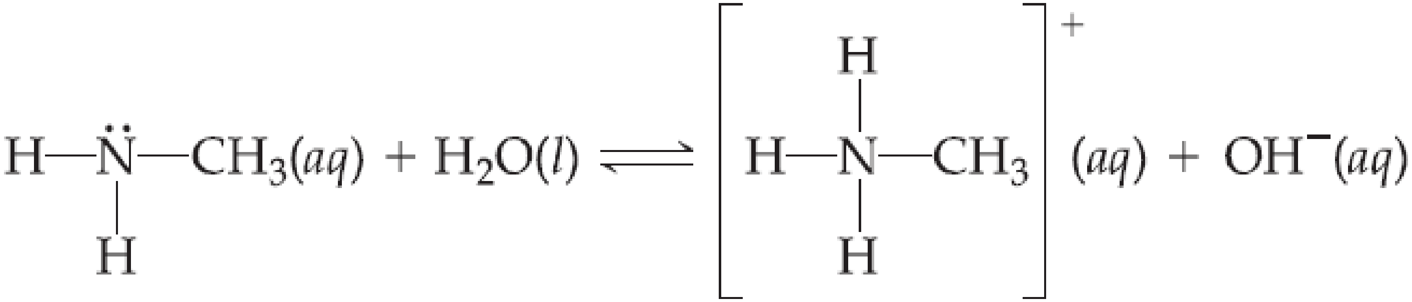
$$x^2 = (0.15)(1.8 \times 10^{-5}) = 2.7 \times 10^{-6}$$

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

Comment: You may be asked to find the pH of a solution of a weak base. Once you have found $[OH^-]$, you can proceed as in Sample Exercise 16.9, where we calculated the pH of a strong base. In the present sample exercise, we have seen that the 0.15 *M* solution of NH_3 contains $[OH^-] = 1.6 \times 10^{-3}$ *M*. Thus, $pOH = -\log(1.6 \times 10^{-3}) = 2.80$, and $pH = 14.00 - 2.80 = 11.20$. The pH of the solution is above 7 because we are dealing with a solution of a base.

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.



$$\mathrm{H{-}}\underset{\underset{\mathrm{H}}{|}}{\ddot{\mathrm{N}}}\mathrm{{-}CH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \left[\mathrm{H{-}}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}}\mathrm{{-}CH_3}\right]^+(aq) + \mathrm{OH^-}(aq)$$

The chemical formula for the conjugate acid of methylamine is usually written $CH_3NH_3^+$.

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

$$\mathrm{ClO^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HClO}(aq) + \mathrm{OH^-}(aq) \quad K_b = 3.3 \times 10^{-7}$$

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

We can calculate [OH^-] by using the right Equation; we will use the latter method here:

$$pOH = 14.00 - pH = 14.00 - 10.50 = 3.50$$

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

This concentration is high enough that we can assume that Equation 16.37 is the only source of OH^-; that is, we can neglect any OH^- produced by the autoionization of H_2O.

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

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

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

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

Thus

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

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

16.8

Relationship Between K_a and K_b

To see if we can find a corresponding quantitative relationship, lets consider the NH_4^+ and NH_3 conjugate acid-base pair. Each of these species reacts with water:

$$\begin{array}{rcl} NH_4^+(aq) & \rightleftharpoons & NH_3(aq) + H^+(aq) \\ NH_3(aq) + H_2O(l) & \rightleftharpoons & NH_4^+(aq) + OH^-(aq) \\ \hline H_2O(l) & \rightleftharpoons & H^+(aq) + OH^-(aq) \end{array}$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_a \times K_b = \left(\frac{[NH_3][H^+]}{[NH_4^+]}\right)\left(\frac{[NH_4^+][OH^-]}{[NH_3]}\right)$$

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

$\boldsymbol{K_a}$ and $\boldsymbol{K_b}$ are related in this way:

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

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

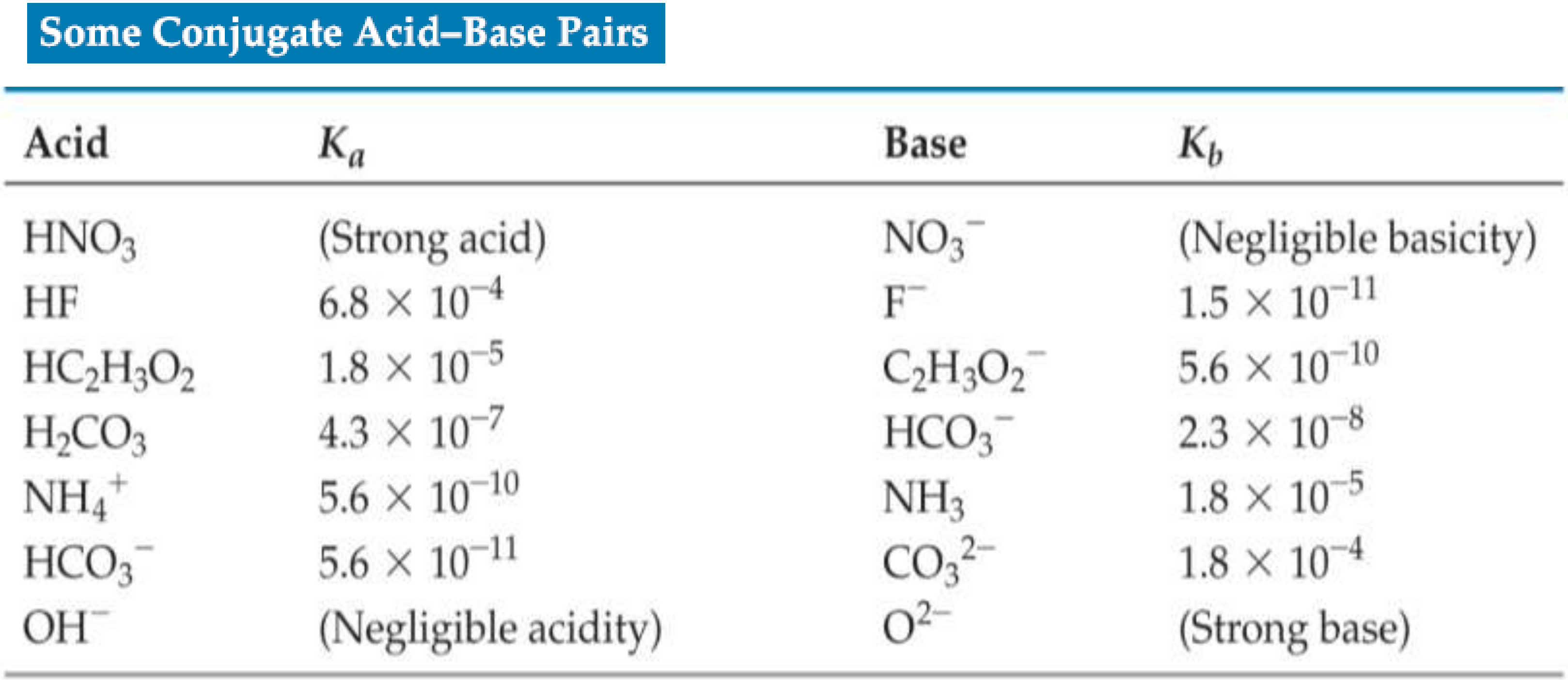
This relationship is so important that it should receive special attention: The product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base equals the ion-product constant for water.

$$K_a \times K_b = K_w$$

As the strength of an acid increases (larger $\boldsymbol{K_a}$), the strength of its conjugate base must decrease (smaller $\boldsymbol{K_b}$) so that the product $\boldsymbol{K_a}$ **x** $\boldsymbol{K_b}$ equals 1.0 x 10^{-14} at 25 ^{o}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:

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



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}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

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

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

Solution

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

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

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

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

16.9

Acid-Base Properties of Salt Solutions

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 H^+(aq) or OH^-(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.

$$\mathbf{B^- + H_2O \rightleftharpoons BH + OH^-}$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

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

$$\mathbf{A^+ + H_2O \rightleftharpoons AOH + H^+}$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

5. 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) NH_4Cl solution is acidic (pH = 3.5)
(c) NaClO solution is basic (pH = 9.5)

This Figure demonstrates the influence of several salts on pH.

Salt:	$NaNO_3$	$Ca(NO_3)_2$	$Zn(NO_3)_2$	$Al(NO_3)_3$
Indicator:	Bromthymol blue	Bromthymol blue	Methyl red	Methyl orange
Estimated pH:	7.0	6.9	5.5	3.5

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, $\boldsymbol{k_a}$ and $\boldsymbol{k_b}$ 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 1st or 2nd 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)** $Ba(CH_3COO)_2$, **(b)** NH_4Cl, **(c)** CH_3NH_3Br, **(d)** KNO_3, **(e)** $Al(ClO_4)_3$.

Solution

(a) This solution contains barium ions and acetate ions. The cation, Ba^{2+}, is an ion of one of the heavy alkaline earth metals and will therefore not affect the pH. The anion, CH_3COO^-, is the conjugate base of the weak acid CH_3COOH and will hydrolyze to produce OH^- ions, thereby making the solution basic .

(b) This solution contains NH_4^+ and Cl^- ions. NH_4^+ is the conjugate acid of a weak base (NH_3) and is therefore acidic. Cl^- is the conjugate base of a strong acid (HCl) and therefore has no influence on the pH of the solution. Because the solution contains an ion that is acidic (NH_4^+) and one that has no influence on pH (Cl^-), the solution of NH_4Cl will be acidic.

(c) This solution contains $CH_3NH_3^+$ and Br^- ions. $CH_3NH_3^+$ is the conjugate acid of a weak base (CH_3NH_2, an amine) and is therefore acidic. is the conjugate base of a strong acid (HBr) and is therefore pH-neutral. Because the solution contains one ion that is acidic and one that is neutral, the solution of CH_3NH_3Br will be acidic.

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

(e) This solution contains Al^{3+} and ClO_4^- ions. Cations, such as Al^{3+}, that are not in groups 1A or 2A are acidic. The ClO_4^- ion is the conjugate base of a strong acid ($HClO_4$) and therefore does not affect pH. Thus, the solution of $Al(ClO_4)_3$ will be acidic.

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

Predict whether the salt Na_2HPO_4 will form an acidic solution or a basic solution on dissolving in water.

Solution

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

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

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

The value of K_a for Equation 16.45, is 4.2×10^{-13}.
We must calculate the value of K_b for Equation 16.46 from the value of K_a for its conjugate acid, $H_2PO_4^-$. We make use of the relationship shown in Equation 16.40.

$$K_a \times K_b = K_w$$

We want to know K_b for the base HPO_4^{2-}, knowing the value of K_a for the conjugate acid HPO_4^{2-}:

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

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

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 HPO_4^{2-} ?

a. H_3PO_4
b. $H_2PO_4^{1-}$
c. PO_4^{3-}
d. HPO_3^{2-}

What is the conjugate acid of SO_4^{2-} ?

a. H_2SO_4
b. HSO_4^{1-}
c. SO_3^{2-}
d. $H_3SO_4^{+}$

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 6.8×10^{-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 6.8×10^{-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. $HClO_2 > HClO > HBrO > HIO$

b. $HClO > HBrO > HIO > HClO_2$

c. $HIO > HBrO > HClO > HClO_2$

d. $HClO_2 > HIO > HBrO > HClO$

Which base is the weakest ?

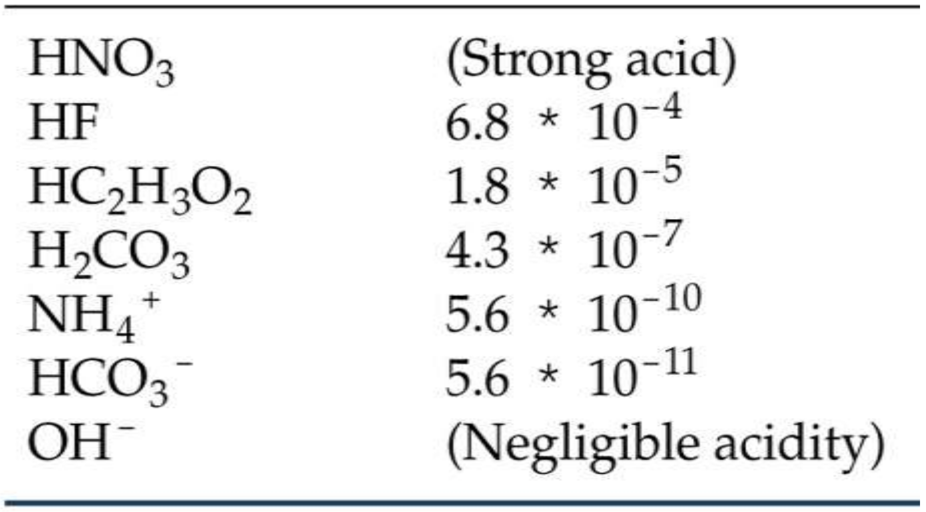
- F^-
- NH_3
- OH^-
- SO_4^{2-}
- $C_2H_3O_2^-$

Which acid is the strongest ?

- H_2O
- H_3O^+
- HF
- $HC_2H_3O_2$
- NH_4^+

Which base is the strongest ?

- NO_3^-
- $C_2H_3O_2^-$
- HCO_3^-
- CO_3^{2-}
- NH_3



Acid	**Ka**
HNO_3	(Strong acid)
HF	$6.8 * 10^{-4}$
$HC_2H_3O_2$	$1.8 * 10^{-5}$
H_2CO_3	$4.3 * 10^{-7}$
NH_4^+	$5.6 * 10^{-10}$
HCO_3^-	$5.6 * 10^{-11}$
OH^-	(Negligible acidity)

If the pH = 2 for an HNO_3 solution, what is the concentration of HNO_3?

- 0.10
- 0.20
- 0.010
- 0.020
- 0.0010

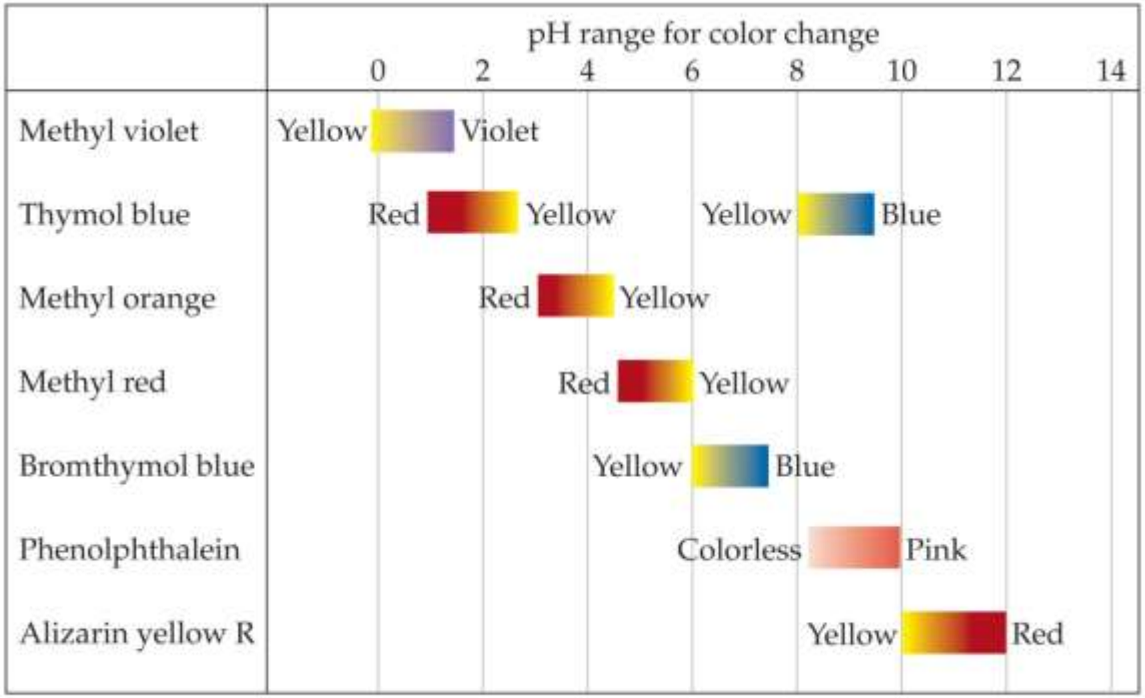
If the pH = 10 for a $Ca(OH)_2$ solution, what is the concentration of $Ca(OH)_2$?

- 1.0×10^{-10}
- 5.0×10^{-11}
- 5.0×10^{-3}
- 1.0×10^{-2}
- 2.0×10^{-2}

a digital pH meter

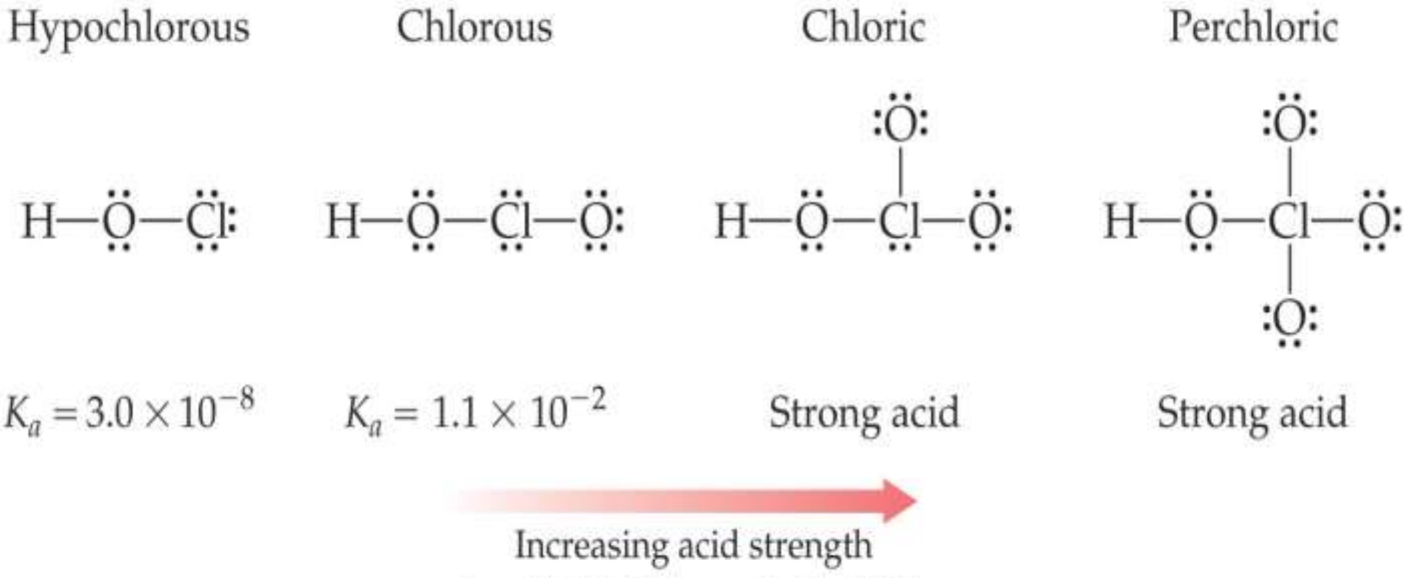
A blue color will result when bromthymol blue is added to an aqueous solution of:

- NH_4Cl
- $KHSO_4$
- $AlCl_3$
- KH_2PO_4
- Na_2HPO_4



What is the pH of a 0.010 *M* $HClO_4$ solution ?

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



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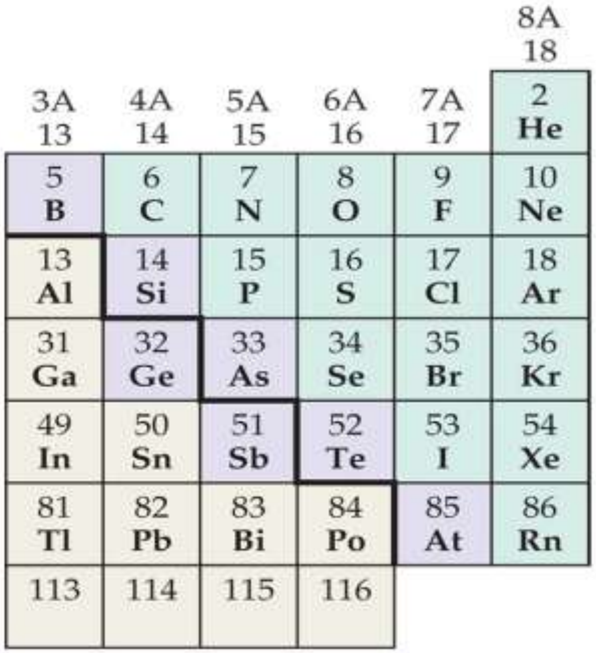
What is the pH of a 0.010 *M* HF solution ?

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

Which acid is the strongest ?

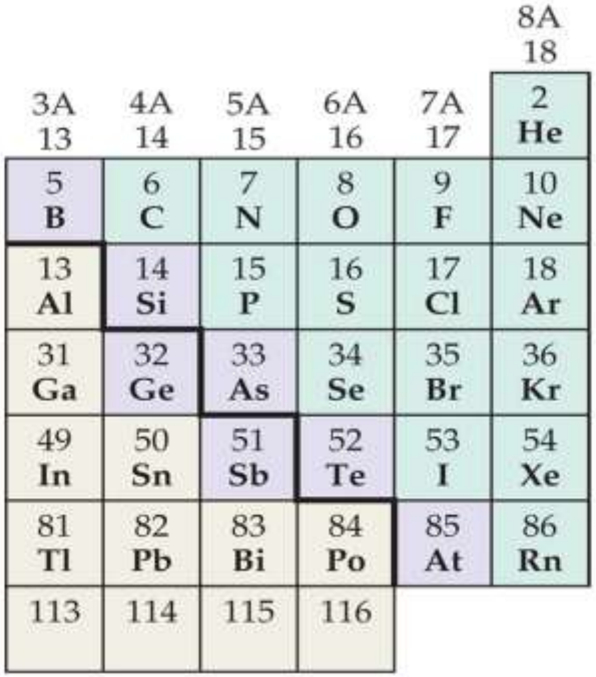
- H_2S
- HF
- HCl
- HBr
- HI



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		

Which base is the strongest ?

- ClO_4^-
- BrO_3^-
- BrO_4^-
- IO_3^-
- IO_4^-

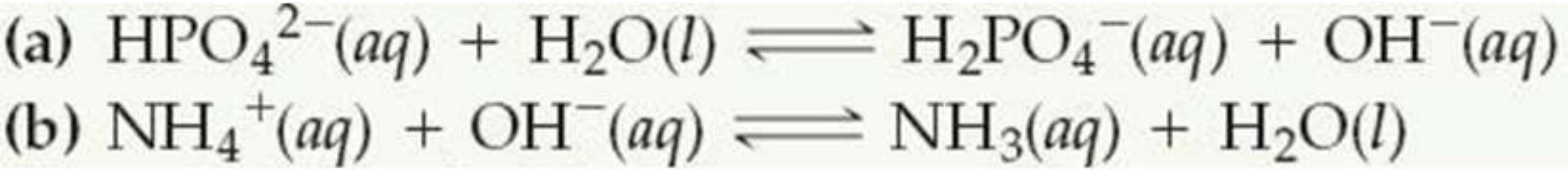


3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
					2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
113	114	115	116		

When lithium oxide (Li_2O) is dissolved in water, the solution turns basic from the reaction of the oxide ion (O_2^-) with water. Write the reaction that occurs, and identify the conjugate acid–base pairs.

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

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



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

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

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

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

Answers: **(a)** $5 \times 10^{-9}\ M$

(b) $1.0 \times 10^{-7}\ M$

(c) $1.0 \times 10^{-8}\ M$

(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?

Answers: **(a)** 3.42,

(b) $[H^+] = 5.3 \times 10^{-9}$ *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 HNO_3 has a pH of 2.34. What is the concentration of the acid?

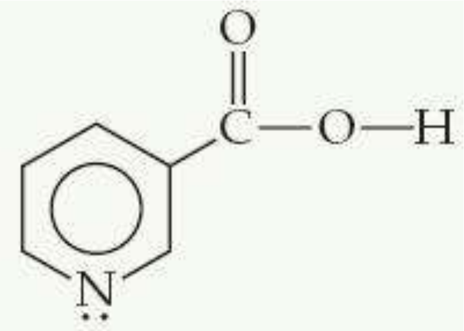
Answer: 0.0046 *M*

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

Answers: **(a)** 7.8×10^{-3} *M*

(b) 2.4×10^{-3} *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: 1.5×10^{-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 *Ka* for niacin (Practice Exercise 16.10) is 1.5 × 10^{-5}. What is the pH of a 0.010 *M* solution of niacin?

Answer: 3.41

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

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

(a) Calculate the pH of a 0.020 *M* solution of oxalic acid ($H_2C_2O_4$). (See Table 16.3 for K_{a1} and K_{a2}.)

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

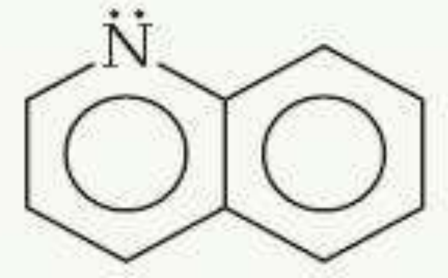
Answers: **(a)** pH = 1.80 ,

(b) $[C_2O_4{}^{2-}] = 6.4 \times 10^{-5}$ *M*

A solution of 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: NO_2^-, PO_4^{3-}, or N_3^-? **(b)** The base quinoline has the following structure: Its conjugate acid is listed in handbooks as having a pK_a of 4.90. What is the base dissociation constant for quinoline?



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

(b) 7.9×10^{-10}

In each of the following, indicate which salt in each of the following pairs will form the more acidic (or less basic) 0.010 *M* solution: **(a)** $NaNO_3$, or $Fe(NO_3)_3$; **(b)** KBr, or KBrO; **(c)** CH_3NH_3Cl, or $BaCl_2$, **(d)** NH_4NO_2, or NH_4NO_3.

Answers: **(a)** $Fe(NO_3)_3$, **(b)** KBr,
(c) CH_3NH_3Cl, **(d)** NH_4NO_3

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

Answer: acidic


Thank You!