CHAPTER 16: Acids and Bases

Figure to come
Collection of household acids and bases?
Effect of acids on fish?
Incorporate pH? Include molecular models?

Caption to come

Chapter 16

Chapter In Context

This chapter continues our discussion of chemical equilibria, applying the concepts and techniques developed in Chapter 15 to the chemistry of acids and bases. In upcoming chapters we will continue to study chemical equilibria as it applies to acid-base reactions, buffers, and the chemistry of sparingly soluble compounds.

Acids and bases control the properties of substances all around us. This goes beyond chemistry to almost all areas of science and technology. Some examples include:

- Biology: Can food "cook" at room temperature? Ceviche is a dish prepared by marinating fish in a citrus solution usually containing lime or lemon juice. The acidic nature of the marinate "cooks" the fish by denaturing proteins, leaving the flesh firm and opaque as if it had been cooked using heat. All proteins are affected by exposure to strong acids or bases, including enzymes, specialized proteins that catalyze metabolic reactions. For example, two of the enzymes that help break down food proteins during digestion are active under very different conditions. Pepsin, the digestive enzyme secreted in the stomach, is most active under the very acidic conditions found in the stomach (pH 1.5), and is completely inactive when the pH is above 6. Trypsin, another digestive enzyme, is found in the intestines and is most active under basic conditions (pH 7.7) and completely inactive under the strongly acidic conditions found in the stomach.
- Environmental Studies: Studies have shown that even a small change in the pH of a lake or river can kill plants and animals. Most trout species cannot reproduce if the pH drops below 5, and a pH less than 4.5 will kill adult trout. Strongly acidic conditions in lakes and rivers also affect the concentration of metal ions in the water such as aluminum. High aluminum concentrations affect fish by clogging their gills, resulting in death by suffocation.
- In Your Home: Did you ever wonder why ammonia is found in so many cleaning products? Most household cleaners contain bases such as ammonia, sodium hydroxide or ethanolamine that help dissolve acidic, greasy solids. Acidic cleaning products will remove lime and rust stains (basic metal oxides and hydroxides).

Chapter Goals

- Use the Brønsted-Lowry acid and base definitions.
- Understand the consequences of water autoionization.
- Apply the principles of aqueous equilibria to acids and bases in aqueous solution.
- Identify the acid-base properties of aqueous salt solutions.
- Recognize the influence of chemical structure and bonding on acid-base properties.

16.1 Introduction to Acids and Bases

OWL Opening Exploration
16.1 Acidity/Basicity of Household Chemicals

Acids and bases are important components in household products, industrial processes, and in environmental and biological systems. As shown in OWL Activity 16.1, many of the items you might find in your home are acids and bases. We begin our study of acids and bases where we left off in Chapter 5, with the Arrhenius acid and base definitions.

Flashback
5.XX Acids and Bases

Arrhenius Acid: A substance containing hydrogen that, when dissolved in water, increases the concentration of H$^+$ ions.
Arrhenius Base: A substance containing the hydroxide group that, when dissolved in water, increases the concentration of OH$^-$ ions.

The Brønsted-Lowry definition is a broader description of the nature of acids and bases. This definition allows us to define a larger number of compounds as acids or bases and to describe acid-base reactions that take place in solvents other than water (such as ethanol or benzene, for example). Ammonia (NH_3) is not an Arrhenius base (its formula does not contain a hydroxide group) but it is defined as a Brønsted-Lowry base when it accepts a proton from an acid such as HCl.

Brønsted-Lowry Acid: A substance that can donate a proton (H$^+$ ion).
Brønsted-Lowry Base: A substance that can accept a proton (H$^+$ ion).

The Lewis acid-base definitions are broader still and are often used to describe reactions that take place in the gas phase. For example, borane (BH_3) is acting as a Lewis acid when it accepts a lone pair from a Lewis base such as ammonia (NH_3).

Lewis Acid: A substance that can accept an electron pair.
Lewis Base: A substance that can donate an electron pair.

Most of the acid-base reactions we will study take place in aqueous solution, so we will use the Brønsted-Lowry definitions when referring to acids and bases. The chemistry of Lewis acids and bases will be discussed in Chapter 18.

OWL Concept Exploration
16.2 Brønsted-Lowry Acids and Bases

Simple Acids and Bases

A Brønsted-Lowry acid-base reaction involves the transfer of a proton from an acid to a base. For example, in the following reaction,

H$^+$ transfer

$$\underset{\text{acid}}{HF(aq)} + \underset{\text{base}}{NH_3(aq)} \rightarrow F^-(aq) + NH_4^+(aq)$$

a proton (H$^+$) is transferred from the acid HF (the proton donor) to the base NH_3 (the proton acceptor). When viewed from the reverse direction,

Flashback
15.1 The Principle of Microscopic Reversibility

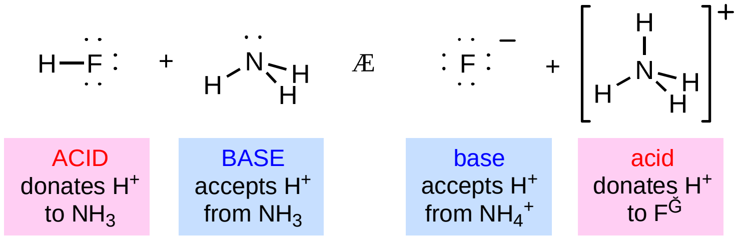
15.XX
Microscopic Reversibility

H$^+$ transfer

$$HF(aq) + \underset{\text{base}}{NH_3(aq)} \leftarrow \underset{\text{acid}}{F^-(aq)} + NH_4^+(aq)$$

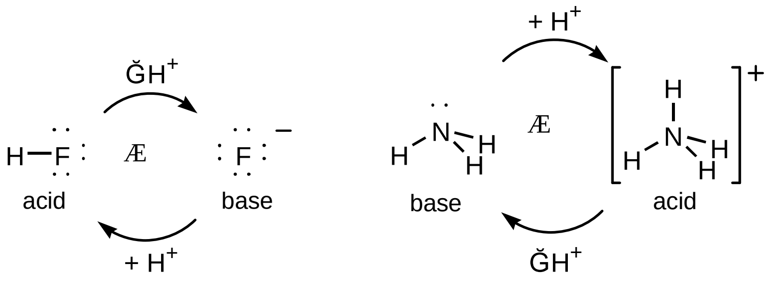
a proton is transferred from the acid (NH_4^+) to the base (F^-). The overall equilibrium is represented as

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



The acid in the forward reaction (HF) and the base in the reverse reaction (F^-) differ only by the presence or absence of H^+ and are called a **conjugate acid-base pair**. The other conjugate acid-base pair in this reaction is NH_4^+/NH_3. Because the Brønsted-Lowry definitions are based on the donating or accepting a proton, every Brønsted-Lowry acid has a conjugate base, every Brønsted-Lowry base has a conjugate acid, and every Brønsted-Lowry acid-base reaction involves two conjugate acid-base pairs.

Chapter Goals Revisited
- Use the Brønsted-Lowry acid and base definitions.
  Identify conjugate acid-base pairs.



EXAMPLE PROBLEM **Acid-base conjugate pairs**

(a) What is the conjugate acid of the iodate ion, IO_3^-?
What is the conjugate base of formic acid, HCO_2H?

(b) Identify the acid, base, conjugate acid, and conjugate base in the following reaction:

$$HCN(aq) + NO_2^-(aq) \rightleftharpoons HNO_2(aq) + CN^-(aq)$$

SOLUTION

(a) IO_3^- accepts a proton to form its conjugate acid, HIO_3:

$$IO_3^-(aq) + H^+(aq) \rightarrow HIO_3(aq)$$

HCO_2H donates a proton to form its conjugate base, HCO_2^-:

$$HCO_2H\ (aq) \rightarrow H^+(aq) + HCO_2^-(aq)$$

(b) In this reaction, the acid (HCN) donates a proton to the base (NO_2^-) resulting in the formation of the conjugate base CN^- and the conjugate acid HNO_2.

H^+ transfer

$$\underset{\text{acid}}{HCN(aq)} + \underset{\text{base}}{NO_2^-(aq)} \rightleftharpoons \underset{\text{conj. acid}}{HNO_2(aq)} + \underset{\text{conj. base}}{CN^-(aq)}$$

OWL Example Problems
16.3 Acid-Base Conjugate Pairs

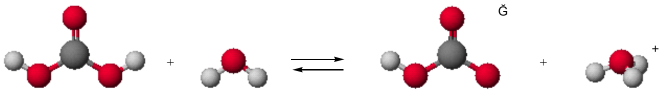
More Complex Acids

The Brønsted-Lowry acids we have seen so far are capable of donating only one proton and are called **monoprotic acids**. **Polyprotic acids** can donate more than one proton.

Carbonic acid, H_2CO_3, is an example of a **diprotic acid**, a polyprotic acid that can donate two protons.

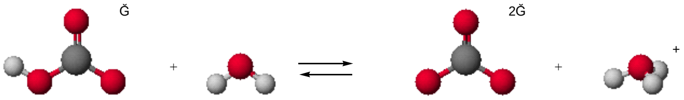
Step 1:

$H_2CO_3(aq) + H_2O(\ell)$ Æ $HCO_3^-(aq) + H_3O^+(aq)$

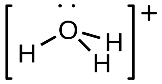


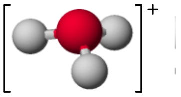
Step 2:

$HCO_3^-(aq) + H_2O(\ell)$ Æ $CO_3^{2-}(aq) + H_3O^+(aq)$



In aqueous solutions the hydronium ion, $H_3O^+(aq)$, is used to represent a hydrated proton, $H^+(aq)$.





Notice that the bicarbonate ion, HCO_3^- can act as a base (accepting a proton to form H_2CO_3) or as an acid (donating a proton to form CO_3^{2-}). We call such species **amphiprotic**. An amphiprotic species is formed when any polyprotic acid loses a proton.

HCO_3^- as an acid: $HCO_3^-(aq) + H_2O(\ell)$ Æ $CO_3^{2-}(aq) + H_3O^+(aq)$

acid base conj. base conj. acid

HCO_3^- as a base: $HCO_3^-(aq) + H_2O(\ell)$ Æ $H_2CO_3(aq) + OH^-(aq)$

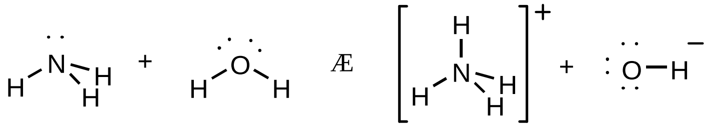
base acid conj. acid conj. base

16.2 Water and the pH Scale

OWL Opening Exploration
16.4 $[OH^-]$ and $[H_3O^+]$ in Aqueous Solution

Because some of the most important acid-base chemistry (including biologically related reactions) occurs in aqueous solution, it is crucial to understand the acid-base nature of water itself. Water is an example of an amphiprotic substance, one that can sometimes act as an acid and at other times as a base in acid-base reactions. For example, you may have noticed that in the bicarbonate ion reactions above, water acted as a base in the first reaction and as an acid in the second.

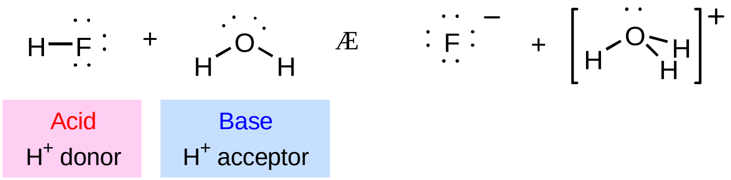
Water acts as an acid, a proton donor, to form the hydroxide ion when it reacts with a base:



Base
H^+ acceptor

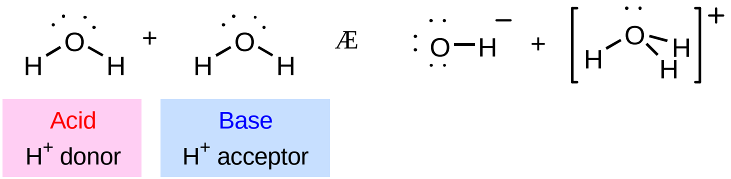
Acid
H^+ donor

Water acts as a base, a proton acceptor, to form the hydronium ion (H_3O^+, a hydrated proton) when it reacts with an acid:



OWL Concept Exploration
16.4a Acid-base hydrolysis reactions

Species such as water that can act either as an acid or as a base can undergo **autoionization**, the reaction between two molecules of a chemical substance to produce ions. Water autoionizes to produce hydronium and hydroxide ions by a proton transfer reaction.



OWL Concept Exploration
16.5 Autoionization

The autoionization of water is a reactant-favored process. Water autoionizes to a very small extent (approximately two out of every billion water molecules in a sample of pure water undergo autoionization) and it is a very weak electrolyte.

$$2\ H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} << 1$$

Equilibrium expressions do not include the concentration of pure liquids or solvents, so this expression can be simplified by including the essentially constant $[H_2O]$ in the equilibrium constant:

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

Flashback
15.2 Writing Equilibrium Constant Expressions

15.X
Writing Equilibrium Constant Expressions

This process is so important that the equilibrium constant is given a special designation and is known as the **ionization constant for water, K_w**, As is true for all equilibrium constants, K_w varies with temperature.

OWL Concept Exploration
16.6 Autoionization and Temperature

At 25 °C,

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \qquad (16.1)$$

In pure water the autoionization of two water molecules produces one H_3O^+ ion and one $OH^–$ ion. Thus, in pure water $[H_3O^+] = [OH^–]$, and at 25 ºC,

$$K_w = [H_3O^+][OH^–] = [H_3O^+]^2 = 1.0 \text{ x } 10^{–14}$$

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

In an acidic or basic solution $[H_3O^+]$ is not equal to $[OH^–]$. According to Le Chatelier's principle, addition of an acid to pure water will increase $[H_3O^+]$, shift the autoionization equilibrium to the left and decrease $[OH^–]$. Addition of a base to pure water will have the opposite effect, increasing $[OH^–]$ and decreasing $[H_3O^+]$. Thus we can make the following generalizations about aqueous solutions at 25 ºC:

In a neutral solution,

$[H_3O^+] = [OH^–] = 1.0 \times 10^{–7}$ M

In an acidic solution,

$[H_3O^+] > [OH^–]$

$[H_3O^+] > 1.0 \times 10^{–7}$ M and $[OH^–] < 1.0 \times 10^{–7}$ M

In a basic solution,

$[OH^–] > [H_3O^+]$

$[H_3O^+] < 1.0 \times 10^{–7}$ M and $[OH^–] > 1.0 \times 10^{–7}$ M

Because K_w is a constant, knowing either $[H_3O^+]$ or $[OH^–]$ for any aqueous solution allows the other to be calculated.

To come: image/diagram showing relationship between $[OH^–]$ and $[H_3O^+]$. Bar graph?

Caption:
Notice that acidic and basic solutions both contain the H_3O^+ and $OH^–$ ions. The relative concentrations of these ions determine if the solution is acidic or basic.

Chapter Goals Revisited

- Understand the consequences of water autoionization.
  Use K_w to calculate $[OH^–]$, $[H_3O^+]$, pH, and pOH.

EXAMPLE PROBLEM **Calculations involving K_w**

A solution at 25 ºC has a hydronium ion concentration of $4.5 \times 10^{–4}$ M.

(a) What is the hydroxide ion concentration in this solution?

(b) Is the solution acidic or basic?

SOLUTION

(a) $[H_3O^+][OH^–] = 1.0 \times 10^{–14}$

$$[OH^–] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}\text{ M}} = 2.2 \times 10^{-11}\text{ M}$$

(b) In this solution, $[H_3O^+] > [OH^–]$ so the solution is acidic.

OWL Example Problems
16.7 Calculations involving K_w

pH and pOH Calculations

Hydronium ion and hydroxide ion concentrations can vary over a wide range in common solutions. In chlorine bleach, $[H_3O^+]$ is around $10^{–12}$ M, while in vinegar it is closer to $10^{–3}$ M. To more easily work with these values, we use a logarithmic scale called the "p-scale":

$$\text{In general, p}X = –\log X \quad (16.2)$$

$$\text{pH} = –\log[H_3O^+] \quad (16.3)$$

$$\text{pOH} = –\log[OH^–] \quad (16.4)$$

Flashback
5.XX Calculating pH
5.12
pH Calculations

In a neutral aqueous solution at 25 ºC, for example, pH = 7.00.

$$\text{pH} = –\log[H_3O^+] = –\log(1.0 \times 10^{–7}\text{ M}) = 7.00$$

Solving the pH and pOH expressions for hydronium ion and hydroxide ion concentration, respectively, allows calculation of $[H_3O^+]$ and $[OH^–]$ from pH and pOH.

$$[H_3O^+] = 10^{-pH} \qquad (16.5)$$
$$[OH^-] = 10^{-pOH} \qquad (16.6)$$

Finally, we can derive an expression relating pH and pOH for aqueous solutions at 25 ºC.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$
$$pK_w = -\log([H_3O^+][OH^-]) = -\log(1.0 \times 10^{-14})$$
$$pK_w = -\log[H_3O^+] + (-\log[OH^-]) = 14.00$$

Thus,

$$pK_w = pH + pOH = 14.00 \qquad (16.7)$$

Image of pH meter

Figure 16.X A pH meter

As you can see from this equation, acidic solutions (low pH, high $[H_3O^+]$) have a high pOH (low $[OH^-]$) and basic solutions (high pH, low $[H_3O^+]$) have a low pOH (high $[OH^-]$.

Solution pH is measured in the laboratory with a pH meter (Figure 16.X), which uses an electrode whose electrical potential is sensitive to H_3O^+ ions in solution. A pH meter must be carefully calibrated before each use by using solutions of known pH, called buffer solutions.

The diagram below shows the combined set of direct relationships between pH, pOH, $[H_3O^+]$, and $[OH^-]$. Note that it is not possible to directly convert between pH and $[OH^-]$, or directly between pOH and $[H_3O^+]$.

$$\begin{tikzcd}
\mathbf{pH} \arrow[r, shift left, "pOH = 14.00 - pH"] \arrow[d, shift left, "{[H_3O^+] = 10^{-pH}}"] & \mathbf{pOH} \arrow[l, shift left, "pH = 14.00 - pOH"] \arrow[d, shift left, "{[OH^-] = 10^{-pOH}}"] \\
{[H_3O^+]} \arrow[u, shift left, "{pH = -\log[H_3O^+]}"] \arrow[r, shift left, "{[OH^-] = K_w/[H_3O^+]}"] & {[OH^-]} \arrow[u, shift left, "{pOH = -\log[OH^-]}"] \arrow[l, shift left, "{[H_3O^+] = K_w/[OH^-]}"]
\end{tikzcd}$$

When doing calculations that involve logarithms, the number of significant figures in the result of the log operation is indicated by the number of digits following the decimal point. For example, log(29) = 1.46 not 1.5. See Appendix X for information on logarithms and significant figures.

OWL Concept Exploration
16.8 pH Relationships

EXAMPLE PROBLEM **pH and pOH calculations**

(a) The hydronium concentration in an aqueous solution of HCl is 4.4×10^{-2} M. Calculate $[OH^-]$, pH, and pOH for this solution.

(b) The pH of an aqueous solution of NaOH is 10.73. Calculate $[H_3O^+]$, $[OH^-]$, and pOH for this solution.

SOLUTION

(a) Rearrange the K_w expression, solving for $[OH^-]$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-2}\ \text{M}} = 2.3 \times 10^{-13}\ \text{M}$$

Example problem, continued

Use $[H_3O^+]$ and $[OH^-]$ to calculate pH and pOH

$$pH = -\log[H_3O^+] = -\log(4.4 \times 10^{-2}\ M) = 1.36$$
$$pOH = -\log[OH^-] = -\log(2.3 \times 10^{-13}\ M) = 12.64$$

As a final check, verify that pH + pOH = 14.00

$$pH + pOH = 1.36 + 12.64 = 14.00$$

(b) Use the rearranged pH equation to calculate $[H_3O^+]$ in this solution.

$$[H_3O^+] = 10^{-pH} = 10^{-10.73} = 1.9 \times 10^{-11}\ M$$

Rearrange the K_w expression, solving for $[OH^-]$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-11}\ M} = 5.3 \times 10^{-4}\ M$$

Because pH + pOH = 14.00,

$$pOH = 14.00 - pH = 14.00 - 10.73 = 3.27$$

OWL Example Problems
16.9 pH and pOH Calculations: Tutorial
16.10 pH and pOH Calculations

16.3 Acid and Base Strength

OWL Opening Exploration
16.11 Percent Ionization

The strength of an acid or base solution depends on two things:

- the concentration of the acid or base, and
- the tendency of the acid or base to donate or accept a proton, respectively.

Strong acids and bases (Table 16.1), as described in Chapter 5, are strong electrolytes that ionize completely in aqueous solution. Not all acids and bases are strong, however. In fact, only a small number of acids and bases are strong; the majority are weak electrolytes and are considered weak acids and weak bases. Only a small fraction of weak acid or weak base molecules are ionized in solution at any moment. For example, less than 1% of acetic acid molecules ionize in a 0.2 M aqueous solution of the acid.

TABLE 16.1 STRONG ACIDS AND STRONG BASES

Strong Acids		**Strong Bases**	
HCl	Hydrochloric acid	LiOH	Lithium hydroxide
HBr	Hydrobromic acid	NaOH	Sodium hydroxide
HI	Hydroiodic acid	KOH	Potassium hydroxide
HNO_3	Nitric acid	$Ca(OH)_2$	Calcium hydroxide (sparingly soluble)
H_2SO_4	Sulfuric acid		
$HClO_4$	Perchloric acid	$Ba(OH)_2$	Barium hydroxide

To come: Figure showing (with molecular models) strong vs. weak acid ionization in aqueous solution

Acid Hydrolysis Equilibria and K_a

The relative strength of a weak acid can be expressed with an equilibrium constant for the reaction of the acid with water. For the weak acid HA,

$$\mathrm{HA(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq)} \qquad K_a = \frac{[\mathrm{H_3O^+}][\mathrm{OH^-}]}{[\mathrm{HA}]} \qquad (16.8)$$

The equilibrium constant for weak acid hydrolysis is given the subscript “a” to indicate that it is an equilibrium constant for a weak acid. The magnitude of K_a, the acid dissociation constant, indicates the relative strength of a weak acid. Acids with larger K_a values are stronger acids that ionize to a greater extent in solution than do acids with smaller K_a values.

Hydrolysis refers to the reaction of a substance with water. You will also see the term “ionization” used to describe this reaction between an acid and water or a base and water. Remember that K_w is called the *ionization constant* for water.

Base Hydrolysis Equilibria and K_b

As we saw for weak acids, the relative strength of a weak base can be expressed with an equilibrium constant for the reaction of the base with water. For the weak base B,

$$\mathrm{B(aq) + H_2O(\ell) \rightleftharpoons HB^+(aq) + OH^-(aq)} \qquad K_b = \frac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]} \qquad (16.9)$$

The equilibrium constant for weak base hydrolysis is given the subscript “b” to indicate that it is an equilibrium constant for a weak base. Like the weak acid K_a values, the magnitude of K_b, the base dissociation constant, indicates the relative strength of a weak base.

OWL Concept Exploration
16.12 Writing K_a and K_b Expressions

Table 16.2 shows K_a and K_b values for some common acids and bases. More extensive tables can be found in the Appendix and in chemistry handbooks. Notice that in Table 16.2,

- The strongest acids have large K_a values and small pK_a values [$pK_a = -\log(K_a)$].
- The strongest bases have large K_b values and small pK_b values [$pK_b = -\log(K_b)$].
- The conjugate base of a strong acid has a very small K_b value. In general, as acid strength (and K_a) increases the strength of the acid’s conjugate base decreases.
- The conjugate acid of a strong base has a very small K_a value. In general, as base strength (and K_b) increases the strength of the base’s conjugate acid decreases.

Strong acid pK_a values (and strong base pK_b values) are very small or even negative. As acid strength decreases, pK_a increases.

Acid	pK_a
HCl	–3
HNO_3	–1.3
CH_3CO_2H	4.7
HCN	9.2

OWL Concept Exploration
16.13 Exploring the Acid-Base Table

TABLE 16.2 K_A AND K_B VALUES

BIG TABLE of K_a and K_b values, something like this, but with K_b values

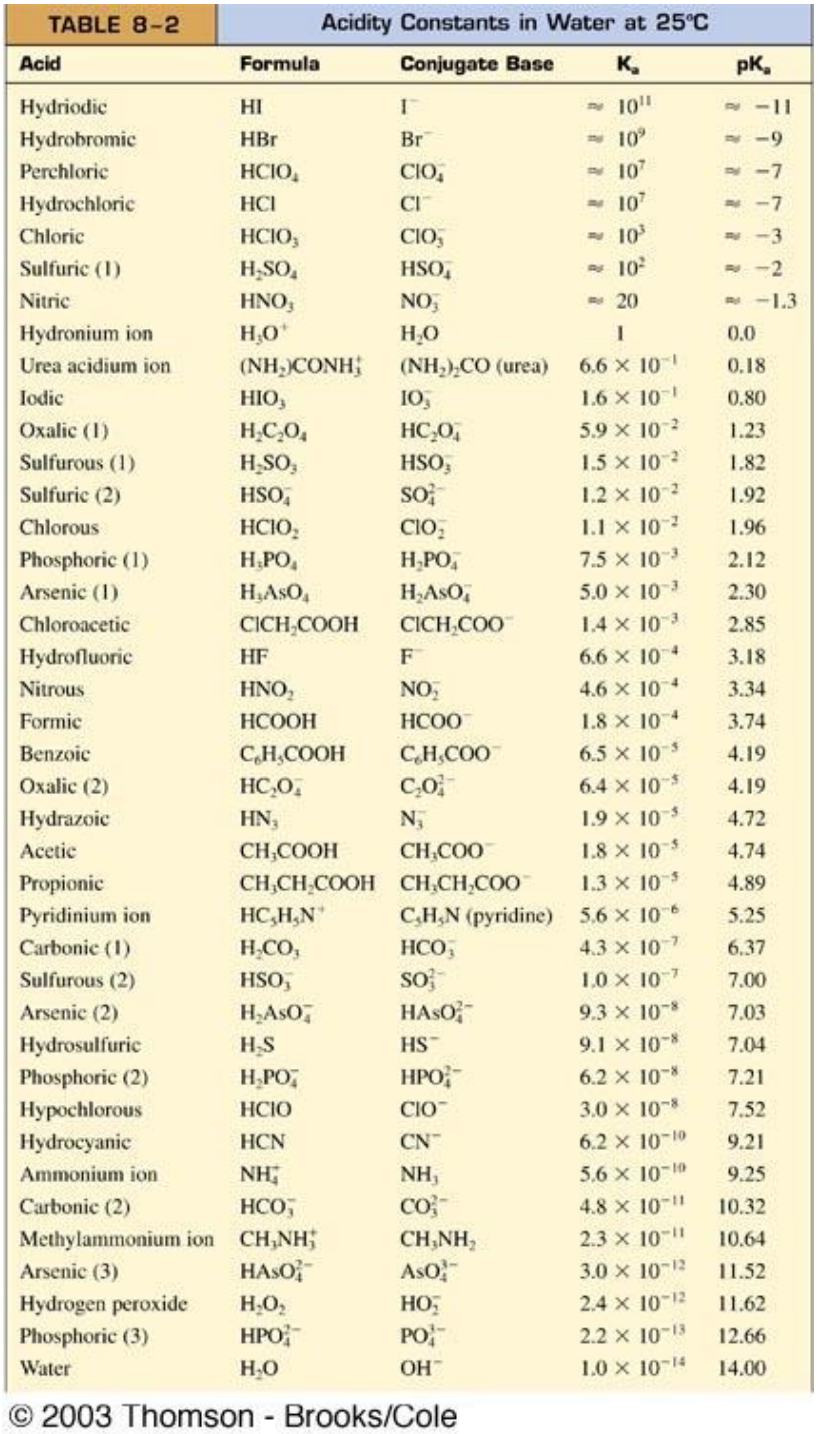


TABLE 8-2 Acidity Constants in Water at 25°C

Acid	Formula	Conjugate Base	K_a	pK_a
Hydriodic	HI	I^-	$\approx 10^{11}$	≈ -11
Hydrobromic	HBr	Br^-	$\approx 10^{9}$	≈ -9
Perchloric	$HClO_4$	ClO_4^-	$\approx 10^{7}$	≈ -7
Hydrochloric	HCl	Cl^-	$\approx 10^{7}$	≈ -7
Chloric	$HClO_3$	ClO_3^-	$\approx 10^{3}$	≈ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\approx 10^{2}$	≈ -2
Nitric	HNO_3	NO_3^-	≈ 20	≈ -1.3
Hydronium ion	H_3O^+	H_2O	1	0.0
Urea acidium ion	$(NH_2)CONH_3^+$	$(NH_2)_2CO$ (urea)	6.6×10^{-1}	0.18
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.5×10^{-2}	1.82
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.5×10^{-3}	2.12
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30
Chloroacetic	$ClCH_2COOH$	$ClCH_2COO^-$	1.4×10^{-3}	2.85
Hydrofluoric	HF	F^-	6.6×10^{-4}	3.18
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Formic	$HCOOH$	$HCOO^-$	1.8×10^{-4}	3.74
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.5×10^{-5}	4.19
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72
Acetic	CH_3COOH	CH_3COO^-	1.8×10^{-5}	4.74
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.3×10^{-5}	4.89
Pyridinium ion	$HC_5H_5N^+$	C_5H_5N (pyridine)	5.6×10^{-6}	5.25
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.0×10^{-7}	7.00
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H_2S	HS^-	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.2×10^{-8}	7.21
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}	7.52
Hydrocyanic	HCN	CN^-	6.2×10^{-10}	9.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	2.3×10^{-11}	10.64
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	3.0×10^{-12}	11.52
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.66
Water	H_2O	OH^-	1.0×10^{-14}	14.00

The Relationship Between K_a and K_b

Table 16.2 shows that as acid strength increases conjugate base strength decreases, and as base strength increases, conjugate acid strength decreases. This relationship can be illustrated mathematically using the K_a and K_b expressions for a conjugate acid-base pair.

Weak acid: $HA(aq) + H_2O(\ell) \rightleftharpoons A^-(aq) + H_3O^+(aq)$

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

Conjugate base: $A^-(aq) + H_2O(\ell) \rightleftharpoons HA(aq) + OH^-(aq)$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Multiplying the two equilibrium expressions and simplifying gives

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$

$$K_a \times K_b = [H_3O^+][OH^-]$$

Therefore,

$$K_a \times K_b = K_w = 1.0 \times 10^{-14} \text{ at } 25\ ^\circ\text{C}$$

Notice that as K_a increases, acid strength increases and K_b for the conjugate base must decrease. Thus stronger acids have weak conjugate bases, and stronger bases have weak conjugate acids. This relationship can be used to determine, for example, the K_b for a weak base if the K_a for the conjugate acid is known.

EXAMPLE PROBLEM The K_a–K_b relationship

Chloroacetic acid, CH_2ClCO_2H, is a weak acid ($K_a = 1.2 \text{ x } 10^{-3}$). What is the value of K_b for its conjugate base, the weak base chloroacetate ion, $CH_2ClCO_2^-$?

SOLUTION

Use the relationship $K_a \times K_b = K_w$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-3}} = 7.7 \times 10^{-12}$$

Chloroacetic acid is a relatively strong weak acid ($K_a \approx 10^{-3}$) so its conjugate base is very weak ($K_b \approx 10^{-11}$).

OWL Concept Exploration
16.14 The K_a–K_b relationship

Determining K_a and K_b values in the laboratory

The K_a and K_b values found in the tables in this book are determined experimentally. One method involves measuring the pH of a solution containing a known concentration of weak acid or a weak base. The information about $[H_3O^+]$ obtained is then used to determine the equilibrium concentrations of all species, and the equilibrium constant for the acid or base hydrolysis. An example is shown below.

EXAMPLE PROBLEM **Determining K_a in the laboratory**

The pH of a 0.086 M solution of nitrous acid (HNO_2) is 2.22. Use this information to determine the value of K_a for nitrous acid.

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

SOLUTION

Step 1. Determine the equilibrium concentration of H_3O^+ from the solution pH.

$$[H_3O^+] = 10^{-pH} = 10^{-2.22} = 0.0060\ M$$

Step 2. Set up an ICE table using the variable x to represent the degree to which the weak acid ionizes, in units of mol/L. Based on the stoichiometry of the hydrolysis reaction, the change in concentration upon weak acid ionization is therefore $-x$ for the acid (HNO_2) and $+x$ for both the conjugate base (NO_2^-) and for H_3O^+. (The initial concentration of H_3O^+ is actually 1.0×10^{-7} M due to the autoionization of water, but this is so small an amount in an acidic solution as to be negligible.)

	$HNO_2(aq) + H_2O(\ell) \rightleftharpoons$	$NO_2^-(aq)$ +	$H_3O^+(aq)$
Initial (M)	0.086	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.086 - x$	x	x

Step 3. The pH measurement tells us the equilibrium concentration of H_3O^+, which is equal to x. We can replace x in the table with that numerical value.

	$HNO_2(aq) + H_2O(\ell) \rightleftharpoons$	$NO_2^-(aq)$ +	$H_3O^+(aq)$
Initial (M)	0.086	0	0
Change (M)	*–0.0060*	*+0.0060*	*+0.0600*
Equilibrium (M)	0.086 – *0.0060*	*0.0060*	*0.0060*

Step 4. The concentrations of all the species are now known at equilibrium, and K_a can be calculated by substituting these in the equilibrium constant expression.

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$$

$$= \frac{(x)(x)}{0.086 - x} = \frac{(0.0060)(0.0060)}{0.086 - 0.0060} = 4.5 \times 10^{-4}$$

OWL Example Problems
16.15 Determining K_a and K_b values: Tutorial
16.16 Determining K_a and K_b values

16.4 Estimating the pH of Acid and Base Solutions

OWL Opening Exploration
16.17 pH of Strong and Weak Acids and Bases

Our knowledge of how different acids act, coupled with our general understanding of equilibria, allow us to perform calculations that make good estimates of solution pH for a wide variety of acid or base solutions.

What about H_2SO_4?
Sulfuric acid is both a strong acid and a diprotic acid. However, it only acts as a strong acid in its first ionization. $K_{a1} >> K_{a2}$

Solutions Containing Strong Acids

Strong acids such as HCl and HNO_3 have large K_a values and are strong electrolytes, ionic compounds that ionize completely in aqueous solution. Therefore, $[H_3O^+]$ in a solution containing a monoprotic strong acid is equal to the concentration of the acid itself. The pH of this solution can be calculated if the strong acid concentration is known. An example of this type of calculation is shown below.

EXAMPLE PROBLEM The pH of a strong acid solution

A solution of nitric acid has $[HNO_3] = 0.028$ M. What is the pH of this solution?

SOLUTION

Nitric acid is a strong acid (assume 100% ionization), so the $[H_3O^+]$ is equal to the initial acid concentration.

$$HNO_3(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

$$[H_3O^+] = [HNO_3]_0 = 0.028 \text{ M}$$

$$pH = -\log[H_3O^+] = -\log(0.028 \text{ M}) = 1.55$$

Notice that K_a is not used in the calculation of a strong acid solution pH.

OWL Example Problems

16.18 Strong Acid pH: Tutorial

Solutions Containing Strong Bases

Strong bases are strong electrolytes, ionic compounds that ionize completely in aqueous solution. Therefore, $[OH^-]$ in a solution containing a strong base is directly related to the concentration of the base itself. The pH of this solution can be calculated if the strong base concentration is known.

EXAMPLE PROBLEM The pH of a strong base solution

What is the pH of a 9.5×10^{-3} M solution of KOH?

SOLUTION

Potassium hydroxide is a strong base (assume 100% ionization), and $[OH^-]$ is equal to the initial base concentration.

$$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$$

$$[OH^-] = [KOH]_0 = 9.5 \times 10^{-3} \text{ M}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{9.5 \times 10^{-3} \text{ M}} = 1.1 \times 10^{-12} \text{ M}$$

$$pH = -\log[H_3O^+] = -\log(1.1 \times 10^{-12} \text{ M}) = 11.98$$

Notice that K_b is not used in the calculation of a strong base pH.

OWL Example Problems

16.19 Strong Base pH: Tutorial

16.20 Strong Acid and Strong Base pH

Solutions Containing Weak Acids

The pH of a solution containing a weak acid can be calculated using the equilibrium constant for the weak acid hydrolysis, K_a. As you saw in Chapter 15, when an equilibrium constant is small we can often assume that the reaction does not proceed to form a significant amount of product. Many weak acids (and weak bases) have very small equilibrium constants, allowing us to simplify the calculation of equilibrium concentrations of reactants and products. Here we use the general rule that, if the value of K_a is small when compared to the initial acid concentration ($[HA]_0 > 100 \cdot K_a$), the amount of weak acid ionized is very small when compared to $[HA]_0$, An example is shown below.

Chapter Goals Revisited

- Apply the principles of aqueous equilibria to acids and bases in aqueous solution.
  Use K_a and K_b to calculate $[OH^-]$, $[H_3O^+]$, pH, and pOH for a weak acid or weak base solution.

Flashback

15.3 Using Equilibrium Constants in Calculations

15.XX Determining Equilibrium Concentrations

EXAMPLE PROBLEM **Weak acid pH (1)**

Calculate the pH of a 0.250 M solution of hypochlorous acid (HClO, $K_a = 3.5 \times 10^{-8}$) and the equilibrium concentrations of the weak acid and its conjugate base.

SOLUTION

Step 1. One of the most important steps in any weak acid or weak base equilibrium problem is the identification of the correct equilibrium. In this case, the correct equilibrium is the weak acid hydrolysis reaction.

$$HClO(aq) + H_2O(\ell) \rightleftharpoons ClO^-(aq) + H_3O^+(aq)$$

Step 2. Determine the initial concentrations of the equilibrium species, assuming the acid has not ionized. The initial acid concentration is equal to the solution concentration, 0.250 M. The initial concentrations of ClO^- and H_3O^+ are zero because no ionization has occurred. (The initial concentration of H_3O^+ is actually 1.0×10^{-7} M due to the autoionization of water, but this is so small an amount in an acidic solution as to be negligible.)

	$HClO(aq) + H_2O(\ell) \rightleftharpoons$	$ClO^-(aq)$	$+\ H_3O^+(aq)$
Initial (M)	0.250	0	0
Change (M)			
Equilibrium (M)			

Step 3. Use the variable *x* to represent the degree to which the weak acid ionizes, in units of mol/L. Based on the stoichiometry of the hydrolysis reaction, the change in concentration upon weak acid ionization is therefore –*x* for the acid (HClO) and +*x* for both the conjugate base (ClO^-) and for H_3O^+.

	$HClO(aq) + H_2O(\ell) \rightleftharpoons$	$ClO^-(aq)$	$+\ H_3O^+(aq)$
Initial (M)	0.250	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)			

Step 4. Complete the table by summing the initial and change in concentrations to arrive at equilibrium expressions for each species. For the acid, it is equal to the initial concentration of the acid minus the amount that ionized (0.250 – *x*). For the conjugate base and hydronium ion, it is equal to the amount of weak acid ionized (*x*).

	$HClO(aq) + H_2O(\ell) \rightleftharpoons$	$ClO^-(aq)$	$+\ H_3O^+(aq)$
Initial (M)	0.250	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.250 - x$	x	x

In the completed ICE table,

x = amount of weak acid ionized
$x = [ClO^-]$ at equilibrium
$x = [H_3O^+]$ at equilibrium

Step 5. Substitute these equilibrium concentrations into the K_a expression.

$$K_a = \frac{[ClO^-][H_3O^+]}{[HClO]}$$

$$= 3.5 \times 10^{-8} = \frac{(x)(x)}{0.250 - x}$$

Because the value of K_a is small when compared to the initial acid concentration ($[HClO]_0 > 100 \cdot K_a$), the amount of weak acid ionized (*x*) is very small when compared to $[HClO]_0$, and the expression can be simplified to

$$K_a = 3.5 \times 10^{-8} = \frac{x^2}{0.250}$$

Solving for *x*, the amount of weak acid ionized and the equilibrium hydronium ion concentration,

$$x = \sqrt{K_a \times 0.250} = 9.4 \times 10^{-5}\ \text{M}$$

$$x = [H_3O^+] = 9.4 \times 10^{-5}\ \text{M}$$

Example problem, continued

Step 6. Use *x*, the equilibrium concentration of H_3O^+ and OCl^-, to calculate the pH of the solution and the equilibrium concentrations of HClO and OCl^-.

$$pH = -\log[H_3O^+] = -\log(9.4 \times 10^{-5}\ M) = 4.02$$

This is a solution containing an acid, so the pH should be less than 7.

$$[OCl^-] = x = 9.4 \times 10^{-5}\ M$$

$$[HClO] = 0.250 - x = 0.250\ M$$

Notice that our assumption (that the amount of weak acid ionized is insignificant when compared to the initial acid concentration) is valid in this case.

It is not always possible to simplify the K_a expression by assuming that *x* is small when compared to the initial acid concentration. In these cases, the weak acid ionization occurs to such an extent that it has a significant effect on the equilibrium concentration and $[HA]_{eq} \neq [HA]_0$. Instead of simplifying the K_a expression you must solve for *x* using the quadratic equation (or a quadratic-solving routine on a calculator).

EXAMPLE PROBLEM Weak acid pH (2)

Calculate the pH of a 0.055 M solution of hydrofluoric acid (HF, $K_a = 7.2 \times 10^{-4}$) and the equilibrium concentrations of the weak acid and its conjugate base.

SOLUTION

Step 1. Write the balanced equation for the hydrolysis reaction.

$$HF(aq) + H_2O(\ell) \rightleftharpoons F^-(aq) + H_3O^+(aq)$$

Step 2. Set up an ICE table for the weak acid hydrolysis reaction. (The initial concentration of H_3O^+ is actually 1.0×10^{-7} M due to the autoionization of water, but this is so small an amount in an acidic solution as to be negligible.)

	$HF(aq) + H_2O(\ell) \rightleftharpoons$	$F^-(aq)$ +	$H_3O^+(aq)$
Initial (M)	0.055	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.055 - x$	x	x

In the completed ICE table,

x = amount of weak acid ionized
$x = [F^-]$ at equilibrium
$x = [H_3O^+]$ at equilibrium

Step 3. Substitute these equilibrium concentrations into the K_a expression.

$$K_a = \frac{[F^-][H_3O^+]}{[HF]}$$

$$= 7.2 \times 10^{-4} = \frac{(x)(x)}{0.055 - x}$$

In this case the value of K_a is significant when compared to the initial acid concentration ($[HF]_0 < 100 \cdot K_a$), and the expression cannot be simplified. Solve for *x* using the quadratic equation.

$$7.2 \times 10^{-4} = \frac{(x)(x)}{0.055 - x}$$

$$7.2 \times 10^{-4}(0.055 - x) = x^2$$

$$0 = x^2 + 7.2 \times 10^{-4}x - 4.0 \times 10^{-5}$$

$$x = \frac{-7.2 \times 10^{-4} \pm \sqrt{(7.2 \times 10^{-4})^2 - 4(1)(-4.0 \times 10^{-5})}}{2(1)}$$

$$x = [H_3O^+] = 6.0 \times 10^{-3}\ M;\ -6.7 \times 10^{-3}\ M$$

Example problem, continued

Step 4. Use the positive root, the equilibrium concentration of H_3O^+, to calculate the pH of the solution and the equilibrium concentrations of HF and F^-.

$$pH = -\log[H_3O^+] = -\log(6.0 \times 10^{-3}\ M) = 2.22$$

This is a solution containing an acid, so the pH should be less than 7.

$$[F^-] = x = 6.0 \times 10^{-3}\ M$$

$$[HF] = 0.055 - x = 0.049\ M$$

Notice that in this case, the amount of weak acid ionized is significant when compared to the initial weak acid concentration.

OWL Example Problems

16.21	*Weak Acid pH: Tutorial*
16.22	*Weak Acid pH*

Solutions Containing Weak Bases

The pH of a weak base solution is calculated using the same method used for weak acid pH calculations. An example is shown below.

EXAMPLE PROBLEM **Weak base pH**

Calculate the pH of a 0.0177 M solution of pyridine (C_5H_5N, $K_b = 1.5 \times 10^{-9}$) and the equilibrium concentrations of the weak base and its conjugate acid.

SOLUTION

Step 1. One of the most important steps in any weak acid or weak base equilibrium problem is the identification of the correct equilibrium. In this case, the correct equilibrium is the weak base hydrolysis reaction.

$$C_5H_5N(aq) + H_2O(\ell) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$$

Step 2. Determine the initial concentrations of the equilibrium species, assuming the base has not reacted with water. The initial base concentration is equal to the solution concentration, 0.0177 M. The concentrations of $C_5H_5NH^+$ and OH^- are zero because no hydrolysis has occurred. (The initial concentration of OH^- is actually 1.0×10^{-7} M due to the autoionization of water, but this is so small an amount in a basic solution as to be negligible.)

	$C_5H_5N(aq) + H_2O(\ell)$	$\rightleftharpoons C_5H_5NH^+(aq)$	$+\ OH^-(aq)$
Initial (M)	0.0177	0	0
Change (M)			
Equilibrium (M)			

Step 3. Use the variable x to represent the degree to which the weak base hydrolyzes, in units of mol/L. Based on the stoichiometry of the hydrolysis reaction, the change in concentration upon weak base hydrolysis is therefore $-x$ for the base (C_5H_5N) and $+x$ for both the conjugate acid ($C_5H_5NH^+$) and for OH^-.

	$C_5H_5N(aq) + H_2O(\ell)$	$\rightleftharpoons C_5H_5NH^+(aq)$	$+\ OH^-(aq)$
Initial (M)	0.0177	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)			

Step 4. Complete the table by summing the initial and change in concentrations to arrive at equilibrium expressions for each species. For the base, it is equal to the initial concentration of the base minus the amount that hydrolyzed ($0.0177 - x$). For the conjugate acid and hydroxide ion, it is equal to the amount of weak base hydrolyzed (x).

	$C_5H_5N(aq) + H_2O(\ell)$	$\rightleftharpoons C_5H_5NH^+(aq)$	$+\ OH^-(aq)$
Initial (M)	0.0177	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.0177 - x$	x	x

Example problem, continued

In the completed ICE table,

x = amount of weak base hydrolyzed
$x = [C_5H_5NH^+]$ at equilibrium
$x = [OH^-]$ at equilibrium

Step 5. Substitute these equilibrium concentrations into the K_b expression.

$$K_b = \frac{[C_5H_5NH^+][OH^{\text{Ğ}}]}{[C_5H_5N]}$$

$$= 1.5 \times 10^{\text{Ğ}9} = \frac{(x)(x)}{0.0177\ \text{Ğ}x}$$

Because the value of K_b is small when compared to the initial base concentration ($[C_5H_5N]_0 > 100 \cdot K_b$), the amount of weak base hydrolyzed (x) is very small when compared to $[C_5H_5N]_0$, and the expression can be simplified to

$$K_b = 1.5 \times 10^{\text{Ğ}9} = \frac{x^2}{0.0177}$$

Solving for x, the amount of weak base hydrolyzed and the equilibrium hydroxide ion concentration,

$$x = \sqrt{K_b \times 0.0177} = 5.2 \times 10^{\text{Ğ}6}\ \text{M}$$

$$x = [OH^-] = 5.2 \times 10^{-6}\ \text{M}$$

Step 6. Use x, the equilibrium concentration of OH^-, to calculate the equilibrium H_3O^+ concentration, the pH of the solution, and the equilibrium concentrations of and $C_5H_5NH^+$.

$$[H_3O^+] = \frac{K_w}{[OH^{\text{Ğ}}]} = \frac{1.0 \times 10^{\text{Ğ}14}}{5.2 \times 10^{\text{Ğ}6}} = 1.9 \times 10^{\text{Ğ}9}\ \text{M}$$

$$\text{pH} = -\log[H_3O^+] = -\log(1.9 \times 10^{-9}\ \text{M}) = 8.71$$

This is a solution containing a base, so the pH should be greater than 7.

$$[C_5H_5NH^+] = x = 5.2 \times 10^{-6}\ \text{M}$$

$$[C_5H_5N] = 0.0177 - x = 0.0177\ \text{M}$$

The assumption that the amount of weak acid hydrolyzed is insignificant when compared to the initial base concentration is correct.

OWL Example Problems
16.23 Weak Base pH: Tutorial
16.24 Weak Base pH

It is not always possible to simplify the K_b expression by assuming that x is small when compared to the initial base concentration. In these cases, the weak base reaction with water occurs to such an extent that it has a significant effect on the equilibrium concentration and $[B]_{eq} \neq [B]_0$. Instead of simplifying the K_b expression you must solve for x using the quadratic equation (or a quadratic-solving routine on a calculator).

16.5 Acid-Base Properties of Salts: Hydrolysis

OWL Opening Exploration
16.25 Hydrolysis of Salts

When you examine a small portion of the table of acids and bases, you can see that many common acids and bases are ionic species.

Insert smaller Acid-Base table with K_a and K_b values

Chapter Goals Revisited

- Identify the acid-base properties of aqueous salt solutions.
  Predict whether an aqueous salt solution is acidic, basic, or neutral.

Notice, for example, that the ammonium ion, NH_4^+, is listed as one of the weak acids, as is the hydrated iron(III) ion, $Fe(H_2O)_6^{3+}$. Similarly, many anions are present in the weak base column, such as the fluoride ion, F^-, and the hypochlorite ion, ClO^-. Salts that contain these ions will mimic these acid-base properties and it is important to be able to predict this behavior. Three general rules can be used to predict acid-base behavior of ions and their salts.

TABLE 16.3 DETERMINING THE ACID-BASE PROPERTIES OF SALTS

1. Anions associated with strong acids and cations associated with strong bases are acid-base neutral.
   Na^+ is the cation associated with the strong base NaOH, and is acid-base neutral. Cl^- is the anion associated with the strong acid HCl, and is acid-base neutral.
2. The conjugate base of a weak acid is itself a weak base, and the conjugate acid of a weak base is itself a weak acid.
   The $CH_3CO_2^-$ anion is the conjugate base of acetic acid and is a basic anion.
   The NH_4^+ cation is the conjugate acid of ammonia and is an acidic cation.
3. Small, highly charged (+2 or +3) metal cations are hydrated in water and act as acidic cations.

If the acid-base properties of each ion are known then the acid-base nature of the salt that contains those ions can be predicted using the following guidelines:

- If both the cation and anion are neutral, the salt is neutral.
- If only one ion is neutral, the other ion controls the acid-base nature of the salt.
  If either the cation or anion is acidic and the other is neutral, the solution is acidic.
  If either the cation or anion is basic and the other is neutral, the solution is basic.
- If neither ion is neutral, the acid-base nature of the salt can be determined by comparing the relative values of K_a and K_b for the ions. In this situation, normally the cation is acidic and the anion is basic.
  If K_a (cation) > K_b (anion), then the solution is mildly acidic.
  If K_b (anion) > K_a (cation) then the solution is mildly basic.

EXAMPLE PROBLEM **Acid-Base Properties of Salts**

What is the acid-base nature of the following salts?

(a) Potassium nitrite, KNO_2

(b) Ammonium carbonate, $(NH_4)_2CO_3$?

SOLUTION

(a) KNO_2

Step 1. Consider the acid-base properties of the cation.

The potassium ion, K^+, is associated with the strong base KOH. This tells us that potassium ion does not contribute to the acid-base properties of a solution. It is acid-base neutral.

Step 2. Consider the acid-base properties of the anion.

The nitrite ion is the conjugate base of nitric acid, HNO_2, a weak acid. The nitrite ion is therefore a weak base. $K_b(NO_2^-) = 2.2 \times 10^{-11}$

Step 3. Combine to determine the acid-base properties of the salt.

Potassium nitrite contains an acid-base neutral cation and a basic anion. This combination means that KNO_2 is a basic salt.

(b) $(NH_4)_2CO_3$

Step 1. Consider the acid-base properties of the cation.

The ammonium ion, NH_4^+, is the conjugate acid of ammonia, NH_3, a weak base. The ammonium ion is therefore a weak acid. $K_a(NH_4^+) = 5.6 \times 10^{-10}$

Step 2. Consider the acid-base properties of the anion.

The carbonate ion is the conjugate base of the bicarbonate ion, HCO_3^-, a weak acid (and an amphiprotic species). The carbonate ion is therefore a weak base. $K_b(CO_3^{2-}) = 2.4 \times 10^{-8}$

Step 3. Combine to determine the acid-base properties of the salt.

Ammonium carbonate contains an acidic cation and a basic anion. Here, $K_b(CO_3^{2-}) > K_a(NH_4^+)$. This combination means that NH_4CO_3 is a basic salt.

OWL Example Problems
16.26 Acid-Base Hydrolysis
16.27 Acid-Base Properties of Salts: Tutorial
16.28 Identifying Acidic and Basic Salts

Determining pH of a Salt Solution

The pH of a solution containing a salt can be calculated by first considering the acid-base nature of the ions of the salt and then using the procedures outlined in Section 3 above for calculating the pH of weak acid and weak base solutions. An example is shown below.

EXAMPLE PROBLEM **pH of Salt Solutions**

What is the pH of a 0.25 M solution of sodium hypochlorite, NaClO?

SOLUTION

Step 1. Determine the acid-base nature of the salt.

The Na^+ ion is an acid-base neutral cation, as are all Group 1A cations. The ClO^- ion is the conjugate base of the weak acid HClO. It is therefore a weak base ($K_b = 2.9 \times 10^{-7}$). Sodium hypochlorite is a basic salt.

Step 2. Write the equation for the hydrolysis of the basic anion. Na^+ is a spectator ion and is not shown in the reaction.

$ClO^-(aq) + H_2O(\ell)$ Æ $HClO(aq) + OH^-(aq)$

Step 3. Use the method shown earlier to set up an ICE table for a weak base hydrolysis reaction.

	$ClO^-(aq) + H_2O(\ell)$ Æ	$HClO(aq)$ +	$OH^-(aq)$
Initial (M)	0.25	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.25 - x$	x	x

Example problem, continued

Substitute the equilibrium concentrations into the K_b expression.

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]}$$

$$= 2.9 \times 10^{-7} = \frac{(x)(x)}{0.25 - x}$$

Because the value of K_b is small when compared to the initial base concentration ($[ClO^-]_0 > 100 \cdot K_b$), the amount of weak base hydrolyzed (x) is very small when compared to $[ClO^-]_0$, and the expression can be simplified to

$$K_b = 2.9 \times 10^{-7} = \frac{x^2}{0.25}$$

Solve for x, the amount of weak base hydrolyzed and the equilibrium hydroxide ion concentration,

$$x = \sqrt{K_b \times 0.25} = 2.7 \times 10^{-4}\ M$$

$$x = [OH^-] = 2.7 \times 10^{-4}\ M$$

Step 4. Use x, the equilibrium concentration of OH^-, to calculate the equilibrium H_3O^+ concentration and the pH of the solution.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.7 \times 10^{-4}} = 3.7 \times 10^{-11}\ M$$

$$pH = -\log[H_3O^+] = -\log(3.7 \times 10^{-11}\ M) = 10.43$$

OWL Example Problems
16.29 pH of Salt Solutions

16.6 Molecular Structure and Control of Acid-Base Strength

OWL Opening Exploration
16.30 Molecular Structure and Acid Strength

In the preceding sections we have described the properties of acids and bases and how to determine the pH of an aqueous solution containing an acid or base. We will now turn to an explanation of what makes one compound more acidic or basic than another. We will restrict this analysis to the control of acid strength, but a similar analysis can be performed to describe base strength.

In a Brønsted-Lowry acid-base reaction, an acid donates a proton to a base:

$$H{-}A + Base \rightarrow [H{-}Base]^+ + A^-$$

When this type of reaction takes place, two different events occur. First, the H—A bond is broken, and second, the group directly attached to the acidic hydrogen in the acid accepts both electrons from the H—A bond, gaining a negative charge in the process. This stepwise process allows us to identify two factors that can control acid strength:

1. Molecules with weaker H—A bonds tend to be stronger acids.
2. Molecules in which the group of atoms (—A) attached to the acidic hydrogen has a high electron–accepting ability tend to be stronger acids.

There are two types of acids that can be used to demonstrate the factors that control acid strength, the HX acids (X = halogen atom) and a series of closely related oxoacids (acids in which the acidic hydrogen is attached to an oxygen atom). The effect of H—X bond energy on the acid strength of the HX acids is shown in Table 16.4.

Table 16.4 Bond Energies and K_a values for the H—X acids

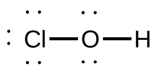
H—X	Bond Energy	K_a
H—F	569 kJ/mol	$\sim 7 \times 10^{-4}$
H—Cl	431 kJ/mol	$\sim 10^{7}$
H—Br	368 kJ/mol	$\sim 10^{9}$
H—I	297 kJ/mol	$\sim 10^{10}$

The order of acid strength for this series

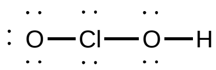
$HF << HCl < HBr < HI$

illustrates the relationship between H—A bond energy and relative acid strength. The compound with the weakest H—A bond is the strongest acid.

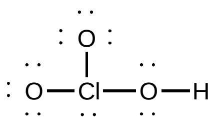
The best illustration of the effect of the electron-accepting ability of a group of atoms on acid strength is seen in a series of oxoacids. For example, the chlorine oxoacids shown here differ only in the number of oxygen atoms attached to the chlorine atom.



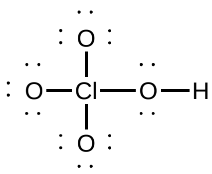
hypochlorous acid



chlorous acid

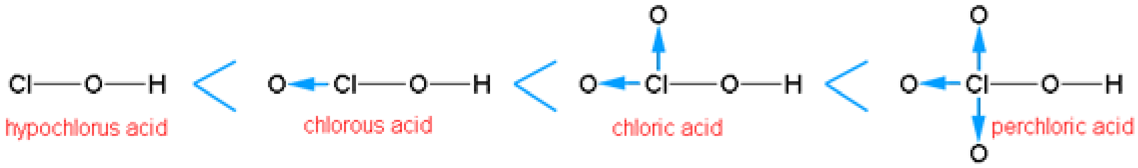


chloric acid



perchloric acid

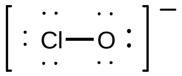
Each additional electronegative oxygen atom increases the electron-accepting ability of the group, drawing electron density away from the Cl atom. This electron-withdrawing effect, also known as the inductive effect, draws electron density away from the oxygen atom bonded to the acidic hydrogen and makes it easier to remove H (as H^+) from the O—H group. As the number of electronegative, electron-withdrawing atoms increases in a series of oxoacids, it becomes easier to lose H^+ from the O—H group and the acid strength increases.

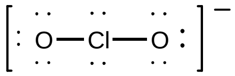


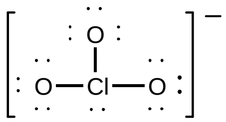
Relative Acid Strength of the Chlorine-Based Oxoacids

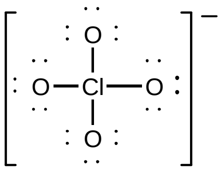
This trend in oxoacid strength can be explained from another perspective where the relative stability of the conjugate base of the weak acid is considered. In general, chemical species that can distribute charge over multiple atoms are more stable than similar species where the charge is concentrated on a single atom or only a few atoms

In the chlorine oxoacid series, each conjugate base carries a –1 charge. In the case of the hypochlorite ion, OCl^-, the negative charge resides primarily on the more electronegative oxygen atom.


hypochlorite ion


chlorite ion


chlorate ion


perchlorate ion

As the number of oxygen atoms increases, the –1 overall charge on the conjugate base is distributed over more and more electronegative oxygen atoms. This distribution of charge means, for example, that the ClO_4^- ion is better able to accommodate the negative charge than the ClO^- ion. As a result, $HClO_4$ is a stronger acid than HClO.

EXAMPLE PROBLEM

Explain, using the relationship between molecular structure and acid strength, why H_2O is a much stronger acid than NH_3.

SOLUTION

The two possible molecular structure explanations are (1) relative strength of the O—H and N—H bonds, and (2) the electron-accepting ability of OH and NH_2 groups.

Possibility 1:		
Bond Energy	N–H	391 kJ/mol
	O–H	463 kJ/mol

The N–H bond is weaker than the O–H bond, so this data suggests that NH_3 should be the stronger acid.

Possibility 2:		
Electronegativity values	N	3.0
	O	3.5

Oxygen is more electronegative than nitrogen, so this data suggests that the OH^- group should be more accommodating of a negative charge than the NH_2^- group.

Overall Conclusion:

The two sets of data contradict each other. The actual trend in acidity observed matches that expected based on the electron-accepting ability argument and is opposite that expected from bond energy data. The greater acidity of H_2O is therefore due to the greater electronegativity of oxygen, and the ability of the conjugate base to better accommodate the negative charge.

OWL Example Problems
16.31 Molecular Structure and Acid Strength

OWL Summary Assignments
16.32 Chapter Review
16.33 Challenging Problems

Key Equations (*will be numbered*)

Section 16.2

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

For aqueous solutions:
In a neutral solution,
$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M
In an acidic solution,
$[H_3O^+] > [OH^-]$
$[H_3O^+] > 1.0 \times 10^{-7}$ M and $[OH^-] < 1.0 \times 10^{-7}$ M
In a basic solution,
$[OH^-] > [H_3O^+]$
$[H_3O^+] < 1.0 \times 10^{-7}$ M and $[OH^-] > 1.0 \times 10^{-7}$ M

$pX = -\log X$

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

$pOH = -\log[OH^-]$

$[H_3O^+] = 10^{-pH}$

$[OH^-] = 10^{-pOH}$

$pH + pOH = 14.00$

Section 16.3

For the weak acid HA, $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

For the weak base B, $K_b = \dfrac{[HB^+][OH^-]}{[B]}$

$K_a \times K_b = K_w = 1.0 \times 10^{-14}$ at 25 °C

Key Terms

Section 16.1
Arrhenius acid
Arrhenius base
Brønsted-Lowry acid
Brønsted-Lowry base
Lewis acid
Lewis base
conjugate acid-base pair
monoprotic acid
polyprotic acid
diprotic acid
amphiprotic

Section 16.2
autoionize
ionization constant for water