

ACID-BASE EQUILIBRIA

The content in this topic is the basis for mastering Learning Objectives 2.2, 3.7, 6.11, 6.12, 6.14, 6.15, and 6.16 as found in the Curriculum Framework.

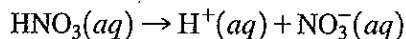
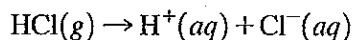
When you finish reviewing this topic, be sure you are able to:

- Predict strong and weak acids and bases from their formulas
- Estimate and calculate quantities such as pH, molar concentrations of various species, and percentage ionization of solutions of strong and weak acids and bases
- Write chemical equations that illustrate the Brønsted–Lowry definition of acids and bases
- Identify acid–base conjugate pairs
- Interconvert K_a and K_b expressions for conjugate pairs
- Construct particle representations for the reactions of acids with bases
- Write and explain equations for acid–base hydrolysis of salt solutions
- Justify with examples why chemical structure affects acid–base behavior

Acids and Bases: A Brief Review

Section 16.1

The **Arrhenius** idea of acids and bases states that acids ionize in water solution to produce hydrogen ions. **Acids are substances that increase the hydrogen ion, H^+ , concentration when dissolved in water.** For example:



Bases are substances that increase the concentration of hydroxide ion, OH^- , when dissolved in water. A base dissociates to produce hydroxide ions in water. Notice in the examples on the next page that sodium hydroxide is “monobasic” and barium hydroxide is “dibasic.” The prefixes mono- and di- refer to the number of available hydroxides in each formula.

Sodium hydroxide is monobasic: $\text{NaOH}(s) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq)$

Barium hydroxide is dibasic: $\text{Ba}(\text{OH})_2(s) \rightarrow \text{Ba}^{2+}(aq) + 2\text{OH}^-(aq)$

Section 16.2 Brønsted–Lowry Acids and Bases

The Brønsted–Lowry theory states:

* Acids are proton (H^+) donors.

* Bases are proton acceptors.

Consider the interaction of hydrogen chloride gas with water. Figure 16.1 shows the same reaction using three different representations: (a) the symbolic chemical equation; (b) Lewis structures representing the species; and (c) a particle model view.

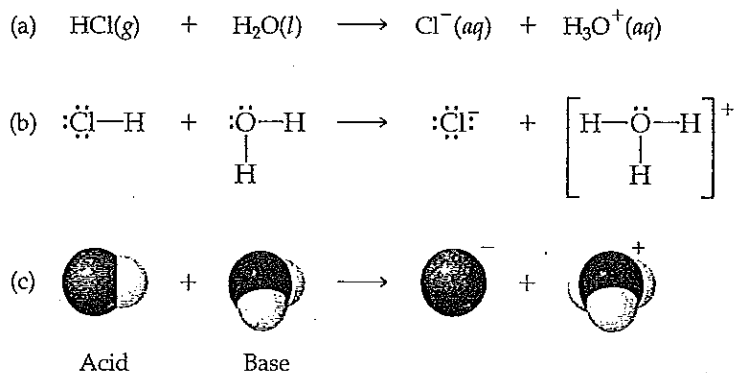


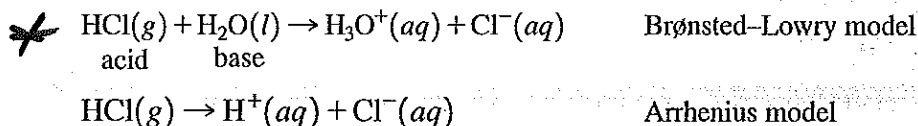
Figure 16.1 Three representations of the reaction of hydrogen chloride with water.

The reaction in Figure 16.1 shows HCl as an acid because it donates a proton to water. H_2O is a base because it accepts a proton.

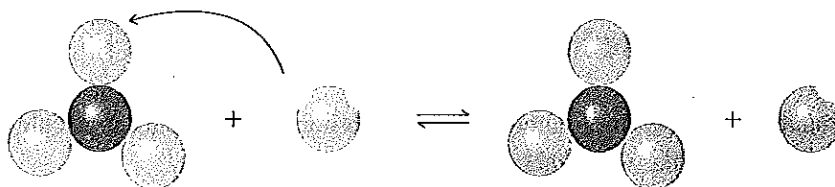
* **Hydronium ion, $\text{H}_3\text{O}^+(aq)$** , is a hydrated proton. When water accepts a proton from an acid, the product is a hydronium ion.

* Notice that when water accepts a proton from HCl, it becomes H_3O^+ . $\text{H}_3\text{O}^+(aq)$ is a hydrated proton called the hydronium ion.

***Common misconception:** Chemists use $\text{H}^+(\text{aq})$ and $\text{H}_3\text{O}^+(\text{aq})$ interchangeably to represent a hydrated proton, the ion responsible for the acidic properties of an aqueous solution. Both of the following equations are chemically equivalent. Notice how one emphasizes the Brønsted–Lowry model and the other represents the Arrhenius model.



*** Sodium carbonate, Na_2CO_3 , is a Brønsted–Lowry base because the carbonate ion accepts a proton from water. Water is an acid because it donates a proton to carbonate ion. Since the sodium ion is a neutral ion, we ignore it in the equation:**



*** Conjugate acid–base pairs** are two substances in aqueous solution whose formulas differ by an H^+ . The acid is the more positive species having the extra H (see Table 16.1).

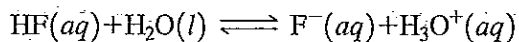
Table 16.1 Examples of acid–base conjugate pairs.

Acid	Base	Equations Involving Acid–Base Conjugate Pairs
NH_4^+ H_2O	NH_3 OH^-	$\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ base acid acid base
H_2SO_3 H_3O^+	HSO_3^- H_2O	$\text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HSO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ acid base base acid

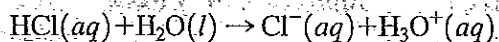
*** Acid–base reactions are reversible reactions. The reversible equations in Table 16.1 illustrate the focus on the transfer of protons according to the Brønsted–Lowry model. In each reaction, there are two sets of acid–base conjugate pairs.**



Common misconception: HF is a weak acid, so F^- is the conjugate base of HF. The reaction of HF with water is expressed as a reversible equilibrium:



However, HCl is a strong acid, so Cl^- is *not* a conjugate base of HCl. The reaction of HCl with water is expressed as an irreversible reaction:

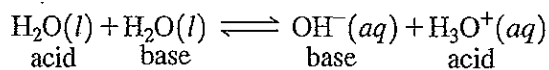
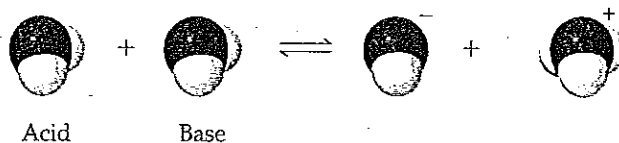
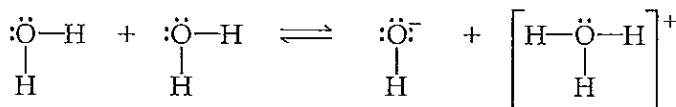
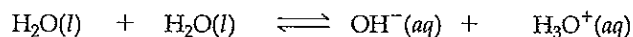


* Because the HCl reaction is not reversible, Cl^- does not accept a proton, and is not a base. The same is true of all anions of strong monoprotic acids.

* An **amphoteric** (also called **amphiprotic**) substance is one that can act as either an acid or a base. Notice in Table 16.1 that water acts as an acid when it transfers a proton to ammonia. Water acts as a base when accepting a proton from sulfuric acid. Water is amphoteric because it can act as an acid or a base.

Section 16.3 The Autoionization of Water

* The **autoionization of water** is a reversible equilibrium where a water molecule transfers a proton to another water molecule.



* Water is both a weak acid and a weak base. It is **amphoteric**. It can act as a proton donor (an acid) or a proton acceptor (a base).

* The **ion product constant** for water, K_w , is the equilibrium constant for the autoionization of water. K_w is a special case of K_c .

$$K_c = K_w = [OH^-][H_3O^+] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C.}$$

The pH Scale

Section 16.4

* Molar concentrations of $\text{H}^+(\text{aq})$ are often expressed as pH, approximated for most solutions as the negative logarithm (base 10) of $[\text{H}^+]$.

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

This mathematical model is accurate for pH values ranging from 2 to 12 and is often used as an approximation for pH values ranging from 0 to 14. Table 16.2 shows the relationships among $[\text{H}^+]$, $[\text{OH}^-]$, pH, and pOH for various solutions.

* **Table 16.2** The pH scale: Relationships among $[\text{H}^+]$, $[\text{OH}^-]$, pH, and pOH.

$[\text{H}^+]$	pH		pOH	$[\text{OH}^-]$
1×10^{-14}	14		0	1×10^{-0}
1×10^{-13}	13		1	1×10^{-1}
1×10^{-12}	12		2	1×10^{-2}
1×10^{-11}	11		3	1×10^{-3}
1×10^{-10}	10		4	1×10^{-4}
1×10^{-9}	9		5	1×10^{-5}
1×10^{-8}	8	basic	6	1×10^{-6}
1×10^{-7}	7	neutral	7	1×10^{-7}
1×10^{-6}	6	acidic	8	1×10^{-8}
1×10^{-5}	5		9	1×10^{-9}
1×10^{-4}	4		10	1×10^{-10}
1×10^{-3}	3		11	1×10^{-11}
1×10^{-2}	2		12	1×10^{-12}
1×10^{-1}	1		13	1×10^{-13}
1×10^{-0}	0		14	1×10^{-14}

* **Common misconception:** It is common to see pH scales ranging from 0 to 14 as illustrated in Table 16.2. However, the assumption that $\text{pH} = -\log[\text{H}^+]$ is valid only for pH values ranging from about 2 through 12. At higher and lower pH values, which represent higher concentrations of acid or base, ion-ion pairing is common and $\text{pH} = -\log[\text{H}^+]$ is invalid.



Table 16.3 shows the mathematical relationships involving pH. Notice that the equations in the left-hand column of Table 16.3 are the logarithmic forms of the equations in the right-hand column.

* **Table 16.3** Mathematical relationships for interconverting $[H^+]$, $[OH^-]$, pH, and pOH.

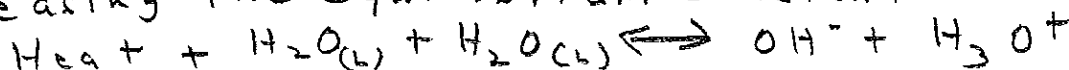
$pH = -\log[H^+]$	$[H^+] = 10^{-pH}$
$pOH = -\log[OH^-]$	$[OH^-] = 10^{-pOH}$
$pH + pOH = 14$	$[H^+][OH^-] = 1 \times 10^{-14}$

Your Turn 16.1

At 0 °C, the ion product constant for water, K_w , is 1.2×10^{-15} .

- Is the autoionization of water an exothermic or endothermic reaction? Explain using a thermochemical equation.
- Calculate the pH of a neutral solution at 0 °C.
- At the human body temperature of 37 °C, will the pH of water be greater or less than 7? Justify your answer.

(a) Because K_w at 0°C is less than K_w at 25°C, the auto-ionization of water is endothermic. If heat is a "reactant" in the thermochemical equation, a decrease in temperature will drive the reaction to the left, decreasing the equilibrium constant



(b) $K_w = [OH^-][H_3O^+] = 1.2 \times 10^{-15}$ at 0°C

$$x^2 = 1.2 \times 10^{-15}$$

$$x = 3.5 \times 10^{-8} = [H_3O^+]$$

Section 16.5 **Strong Acids and Bases**

$$pH = -\log [3.5 \times 10^{-8}] = \boxed{7.46}$$

* **Strong acids and strong bases are strong electrolytes.** Strong acids and strong bases ionize completely in dilute aqueous solution. There are seven common strong acids and eight common strong bases. It is useful to refer to their names and formulas given in Table 16.4. Notice that the strong bases are the hydroxides of the Group 1 alkali metals and the hydroxides of the Group 2 alkaline earth metals. Strong acids and bases are generally, but not always, associated with the Arrhenius model for acids and bases.

(c) The pH of water at 37°C will be less than 7 because at higher Temp. K_w increases so both $[H_3O^+]$ and $[OH^-]$ increase

Table 16.4 The names and formulas of strong acids and strong bases.

Strong Acids		Strong Bases	
sulfuric acid*	H ₂ SO ₄	lithium hydroxide	LiOH
nitric acid	HNO ₃	sodium hydroxide	NaOH
perchloric acid	HClO ₄	potassium hydroxide	KOH
chloric acid	HClO ₃	rubidium hydroxide	RbOH
hydrochloric acid	HCl	cesium hydroxide	CsOH
hydrobromic acid	HBr	calcium hydroxide**	Ca(OH) ₂
hydroiodic acid	HI	strontium hydroxide**	Sr(OH) ₂
		barium hydroxide**	Ba(OH) ₂

*Sulfuric acid is a diprotic acid and only the first proton ionizes completely.

**Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂ are dibasic, which means that two moles of hydroxide ions are produced per formula unit of base that ionizes.

Neutral ions are generally the aqueous anions of strong acids and the aqueous cations of strong bases. Table 16.5 lists the common cations and anions that are neutral in aqueous solution. Generally, most of all other anions are slightly basic and most of all other cations are slightly acidic.

Common misconception: The strong diprotic acid, sulfuric acid, H₂SO₄, does not dissociate completely. Therefore, in an aqueous solution of sulfuric acid, the concentration of the H⁺ ions is not double the concentration of the acid. The same is not true of strong dibasic bases such as calcium hydroxide, which ionize completely in solution. In a solution of calcium hydroxide, Ca(OH)₂, the concentration of the OH⁻ ion is double that of the calcium hydroxide.



Table 16.5 Neutral ions are the aqueous anions of strong acids and the aqueous cations of strong bases.

Neutral Aqueous Anions		Neutral Aqueous Cations	
nitrate	NO ₃ ⁻	lithium ion	Li ⁺
perchlorate	ClO ₄ ⁻	sodium ion	Na ⁺
chlorate	ClO ₃ ⁻	potassium ion	K ⁺
chloride	Cl ⁻	rubidium ion	Rb ⁺
bromide	Br ⁻	cesium ion	Cs ⁺
iodide	I ⁻	calcium ion	Ca ²⁺
sulfate*	SO ₄ ²⁻	strontium ion	Sr ²⁺
		barium ion	Ba ²⁺

*Sulfate ion, SO₄²⁻, is weakly basic.



Common misconception: Although aqueous calcium ion, Ca^{2+} , is the cation of a strong base and is generally considered to be neutral, it does show slightly acidic properties consistent with Lewis acid character and ion pairing.

Your Turn 16.2



Explain why aqueous solutions of each of the following salts are neutral: NaCl , KNO_3 , LiClO_4 , BaBr_2 , CsI . Write your answer in the space provided.

The solutions are neutral because they all contain the cations and anions of strong base and strong acids, respectively.

Sections 16.6 and 16.7

Weak Acids and Weak Bases



Weak acids are acidic substances that only partially ionize in aqueous solution, usually about 1% or less. Weak acids are weak electrolytes. For example, hydrofluoric acid, acetic acid, and nitrous acid are all weak acids. (Each ionizes only partially to establish an equilibrium between the acid and its conjugate base.)

Table 16.6 shows the ionization of some weak acids in water. A comprehensive listing of the ionization constants of weak acids can be found in Appendix D, Table D-1 of *Chemistry: The Central Science*.

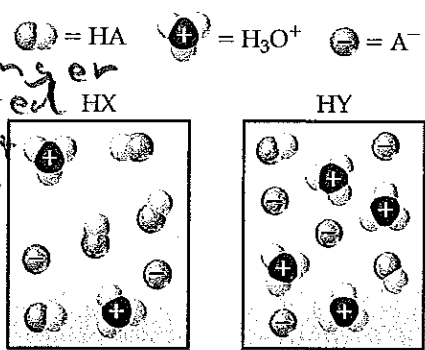
Table 16.6 Ionization of some weak acids in water.

Weak Acid	Conjugate Base	Equilibrium Expression, K_a	Value of K_a
$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$		$K_a = [\text{H}_3\text{O}^+][\text{F}^-]/[\text{HF}]$	6.8×10^{-4}
$\text{HClO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}^-(aq)$		$K_a = [\text{H}_3\text{O}^+][\text{ClO}^-]/[\text{HClO}]$	3.0×10^{-8}
$\text{HIO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{IO}^-(aq)$		$K_a = [\text{H}_3\text{O}^+][\text{IO}^-]/[\text{HIO}]$	2.3×10^{-11}
$\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)$		$K_{a_1} = [\text{H}_3\text{O}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$	4.3×10^{-7}
$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq)$		$K_{a_2} = [\text{H}_3\text{O}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$	5.6×10^{-11}

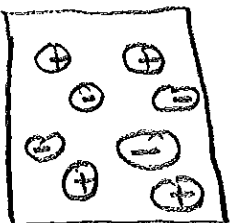
Your Turn 16.3

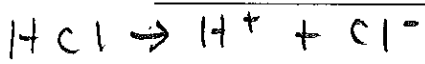
- a. Examine the figure below and identify which acid, HX or HY, is the stronger acid. Justify your answer.
 b. Is either HX or HY a strong acid? Explain your reasoning.
 c. Make a similar sketch to show how the system might look if HCl were the acid. Explain your drawing.
 Write your answers in the space provided.

(a) HY is the stronger acid as reflected by the fact that 4 of its 6 molecules have ionized, whereas only 2 of 6 molecules of HX have ionized.



(b) neither HY or HX have ionized completely, so neither is a strong acid

(c)  all molecules of HCl have ionized.



* Weak bases are also weak electrolytes. Weak bases only partially ionize in solution.

Table 16.7 shows the ionization of some weak bases in water. A comprehensive listing of the ionization constants of weak bases can be found in Appendix D, Table D-2 of *Chemistry: The Central Science*.

Table 16.7 Ionization of some weak bases in water.

Weak Base	Conjugate Acid	Equilibrium Expression, K_b	Value of K_b
$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$		$K_b = [OH^-][NH_4^+]/[NH_3]$	1.8×10^{-5}
$C_5H_5N(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + C_5H_5NH^+(aq)$		$K_b = [OH^-][C_5H_5NH^+]/[C_5H_5N]$	1.7×10^{-9}
$HCO_3^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2CO_3(aq)$		$K_b = [OH^-][H_2CO_3]/[HCO_3^-]$	2.3×10^{-8}
$F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$		$K_b = [OH^-][HF]/[F^-]$	1.5×10^{-11}

- * Weak bases tend to be anions other than anions of strong acids. Neutral nitrogen compounds called amines are also weak bases. Amines have a pair of electrons that can attract protons. Anions have negative charges that can also attract protons.
- * The acid ionization constant, K_a , is the equilibrium constant for the ionization of a weak acid in water.
- * The base ionization constant, K_b , is the ionization constant for a weak base.



- * **Common misconception:** K_a and K_b are not new ideas. The respective subscripts "a" and "b" denote that K_a is a special case of K_c used to specify the ionization of a weak acid in water and that K_b is a special case for a weak base. Also, K_a and K_b are sometimes called the acid dissociation constant and the base dissociation constant, respectively.

- * The value of K_a or K_b indicates the relative extent to which a weak acid or weak base ionizes. For example, the larger the K_a , the greater the extent to which the acid ionizes. When comparing two weak acids, the one with the larger K_a is said to be the "stronger" weak acid. It ionizes to a larger extent. Of the acids listed in Table 16.6, hydrofluoric acid, HF, has the largest K_a , so it ionizes to the greatest extent. HF is said to be the strongest of the weak acids listed. Similarly, of the bases listed in Table 16.7, ammonia, NH_3 , has the largest K_b , so it is the strongest weak base of those listed.

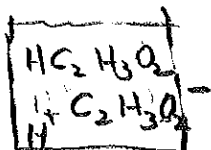
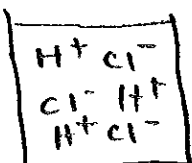
* Your Turn 16.4

← Which acid listed in Table 16.6 is the weakest? Which base listed in Table 16.7 is the weakest? Justify your choices. Write your answers in the space provided.

HIO is the weakest acid on table 16.6 because it has the smallest K_a value.

F^- is the weakest base on table 16.6 because it has the smallest K_b value.

Carbonic acid, H_2CO_3 , is an example of a weak diprotic acid. Table 16.6 shows two ionization constants for carbonic acid. K_{a_1} is the equilibrium constant for the ionization of the first proton. K_{a_2} represents the equilibrium constant for the ionization of the second proton. For all polyprotic acids, the first proton to ionize is always the most readily ionized. The K_a value becomes successively smaller as successive protons are removed, so $K_{a_1} > K_{a_2} > K_{a_3} \dots$



Your Turn 16.5

* Each of two 50 mL solutions has a pH of 5. One contains hydrochloric acid and the other contains acetic acid. Which solution has the higher

- a. concentration of acid? $\rightarrow \text{HC}_2\text{H}_3\text{O}_2$
 b. percentage ionization of acid? HCl
 c. amount of 0.1 M NaOH needed to neutralize the acid? $1 \text{ HC}_2\text{H}_3\text{O}_2$
 d. conductivity? HCl and $\text{HC}_2\text{H}_3\text{O}_2$ are equally conductive.

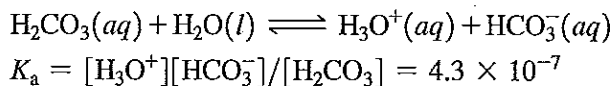
Explain your answers. Write your answers in the space provided.

- (a) acetic acid, a weak acid will require a greater concentration to achieve the same pH as a stronger acid because only about 1% of acetic acid ionizes.
 (b) HCl , a strong acid, ionizes 100%
 (c) Because acetic acid is more concentrated an equal volume requires more base to neutralize all of the acid present.
 (d) Both solutions will have equal conductivity because the ion concentrations are equal.

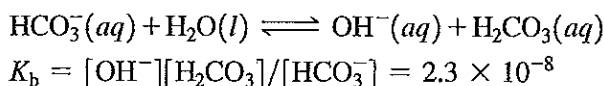
Relationship Between K_a and K_b Section 16.8

* For any conjugate acid-base pair, $K_w = K_a \times K_b$.

Consider, for example, the reaction of carbonic acid with water:



* Hydrogen carbonate ion, HCO_3^- , is the conjugate base of the weak acid, H_2CO_3 . Hydrogen carbonate ion reacts with water according to the following equation:



* K_b for any conjugate base is the ratio of K_w to K_a of the acid:

$$K_b = K_w/K_a = \frac{([\text{OH}^-][\text{H}_3\text{O}^+])}{([\text{H}_3\text{O}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3])}$$

$$= \frac{[\text{OH}^-][\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]}$$

$$K_b = K_w/K_a = 1.0 \times 10^{-14}/4.3 \times 10^{-7} = 2.3 \times 10^{-8}$$



* **Common misconception:** It is customary to tabulate only K_a or K_b for a conjugate pair because, using the relationship, $K_w = K_a \times K_b$, one can be conveniently converted to the other. Typically, only the equilibrium constants for nonionic species appear in a table. For example, the K_b for ammonia, NH_3 , is reported in Appendix D of *Chemistry: The Central Science*, but not the K_a for the conjugate ammonium ion, NH_4^+ . Similarly, the K_a for acetic acid, CH_3COOH , appears in Appendix D, but not the K_b for the conjugate base acetate ion, CH_3COO^- . It is important to be able to recognize the conjugate of any given acid or base and to know how to calculate its corresponding K_a or K_b .

* Recall that water and protonated anions (HCO_3^- , HSO_3^- , H_2PO_4^- , etc.) tend to be amphoteric. That is, they can act as either acids or bases. To tell whether a protonated anion is acidic or basic in water, we can do one of three things: measure the pH of an aqueous solution containing the anion, use an acid–base indicator, or calculate and compare the K_a and K_b of the anion. If the K_a of the anion is larger than its corresponding K_b , the anion forms an aqueous solution that is acidic. If its K_b is larger than its K_a , the solution is basic.

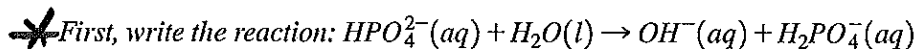
Consider the triprotic acid, phosphoric acid, H_3PO_4 . The sequential ionization of its three protons and the corresponding K_a values are illustrated by the equations in Table 16.8. Notice that two species involved in the equations are amphoteric protonated anions, H_2PO_4^- and HPO_4^{2-} . Their reactions as bases are also illustrated in Table 16.8.

Table 16.8 The ionization of phosphoric acid.

	Acid Ionization	Acid Ionization Constant
1	$\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{H}_2\text{PO}_4^-(aq)$	$K_{a_1} = 7.5 \times 10^{-3}$
2	$\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HPO}_4^{2-}(aq)$	$K_{a_2} = 6.2 \times 10^{-8}$
3	$\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{PO}_4^{3-}(aq)$	$K_{a_3} = 4.2 \times 10^{-13}$
	Base Ionization	Base Ionization Constant
4	$\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_3\text{PO}_4(aq)$	$K_b = K_w/K_{a_1}$
5	$\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{PO}_4^-(aq)$	$K_b = K_w/K_{a_2}$
6	$\text{PO}_4^{3-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HPO}_4^{2-}(aq)$	$K_b = K_w/K_{a_3}$

Example:

Is an aqueous solution of Na_2HPO_4 acidic or basic?

Solution:

Calculate the value of K_b for HPO_4^{2-} and compare it to the value of K_{a3} for HPO_4^{2-} . (Keep in mind that the aqueous sodium ion, $\text{Na}^+(\text{aq})$, is neutral.)

The larger ionization constant will predict the acid-base characteristic of its aqueous solution.

For Equation 5, $K_b = K_w/K_{a2} = 1.0 \times 10^{-14}/6.2 \times 10^{-8} = 1.6 \times 10^{-7}$.

(We use K_{a2} to calculate the K_b for Equation 5 because Equation 5 includes the same conjugate pair as Equation 2.)

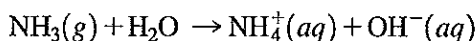
* $K_a = 4.2 \times 10^{-13} < K_b = 1.6 \times 10^{-7}$

Because its K_b is larger than its K_a , HPO_4^{2-} forms a basic solution.

* The Arrhenius and Brønsted–Lowry theories are two different ways of visualizing the same concept. The different classifications lead to different insights in understanding acid–base reactions.

* The Arrhenius model focuses on the ions (H^+ for acids and OH^- for bases) produced in solution. The Brønsted–Lowry model demonstrates acids and bases as proton transfer agents in chemical reactions.

Consider the reaction of ammonia with water:



* Ammonia is clearly an Arrhenius base because it increases the hydroxide ions in solution. It is also a Brønsted–Lowry base because it accepts a proton. Table 16.9 summarizes the major points of the two acid–base theories.

* **Table 16.9** Comparing acid–base models with definitions and examples.

Model	Definition	Example Equation
Arrhenius acid	Increases H^+ in solution	$\text{HCl}(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
Arrhenius base	Increases OH^- in solution	$\text{NaOH}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$
Brønsted acid	Proton donor	$\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$
Brønsted base	Proton acceptor	$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

* **Calculations Involving Strong Acids and Strong Bases**

Table 16.10 shows the mathematical relationships for calculating concentrations of ions in strong and weak acid and base solutions. Although these relationships are useful, understand that they are simply mathematical models for the chemistry that takes place in solutions.

Table 16.10 Mathematical relationships for calculating $[H^+]$ and $[OH^-]$ in strong and weak acid and base solutions.

	Acid	Base
Strong	$x = I$	$y = I$ (monobasic)
		$y = 2 \times I$ (dibasic)
Weak	$K_a = x^2/I$ if $I > 100 K_a$ $K_a \times K_b = K_w = 1 \times 10^{-14}$	$K_b = y^2/I$ if $I > 100 K_b$

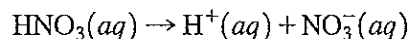
 I = initial molar concentration of acid or base x = the moles per liter of acid that ionizes y = the moles per liter of base that ionizes

$$K_a = \frac{[H^+][X^-]}{[HX]}$$



* **Common misconception:** The most difficult part of performing calculations involving strong and weak acids and bases is recognizing the chemistry. Does the problem involve an acid or a base? Is the acid or base strong or weak? If you can first answer these questions based on the chemistry, then the calculations are less complicated.

* Strong acids ionize completely. Therefore, no equilibrium is established because all the initial concentration of the reactant acid is converted to products. For all strong acids, the ICE tables are the same. For example, the ICE table for the ionization of 0.20 M nitric acid is:



<i>I</i>	0.20	0	0
<i>C</i>	-0.20	+0.20	+0.20
<i>E</i>	0	0.20	0.20

* All the strong acid ionizes, so the initial concentration of the acid is the same as the final concentration of H^+ ion or $x = I$.

Example:

Calculate the $[H^+]$ and pH in a solution of 0.015 M nitric acid, HNO_3 .

Solution:

$$I = x$$

$$[HNO_3] = [H^+] = 0.015 M$$

$$pH = -\log(0.015) = 1.82$$

By similar reasoning, the $[\text{OH}^-]$ of a strong base solution is the same as the concentration of a monobasic strong base and double the concentration of a dibasic strong base.

$I = y$ for monobasic and

$I = 2y$ for dibasic, where $y =$ the moles per liter of base that ionize

Example:

Calculate the $[\text{OH}^-]$ and the pH in a 0.025 M KOH solution and the $[\text{OH}^-]$ and the pH in a 0.025 M $\text{Ba}(\text{OH})_2$ solution.

Solution:

* For the KOH solution,

$$[\text{KOH}] = [\text{OH}^-] = 0.025 \text{ M}$$

$$\text{pOH} = -\log(0.025) = 1.60$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.60 = 12.40$$

* For the $\text{Ba}(\text{OH})_2$ solution,

$$[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2] = 2 \times 0.025 \text{ M} = 0.050 \text{ M}$$

$$\text{pOH} = -\log(0.050) = 1.30$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.30 = 12.70$$

Calculations Involving Weak Acids

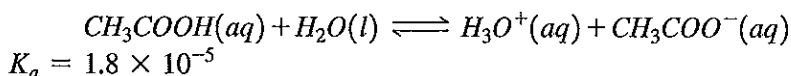
* The ionization of a weak acid in water is a reversible equilibrium, and each weak acid ionization produces the same ICE table.

Example:

* Calculate the pH of a 0.15 M solution of acetic acid, CH_3COOH .

Solution:

First, set up an ICE table for the ionization of an initial concentration of acetic acid, CH_3COOH . Let x equal the number of moles per liter of weak acid that ionizes.



<i>I</i>	<i>I</i>	0	0
<i>C</i>	$-x$	$+x$	$+x$
<i>E</i>	$I - x$	x	x

$$K_a = [\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] = (x)(x)/(I - x)$$

In general, if $I > 100 K_a$, then the assumption $I - x = I$ is a good approximation. Most weak acids have a K_a that is less than 10^{-3} , so I is usually greater than $100 K_a$.

* The equation used for calculations involving the ionization of weak acids simplifies to:

$$K_a = x^2/I$$

* where K_a is the ionization constant for the weak acid, x is the number of moles per liter of weak acid that ionizes, and I is the initial molar concentration of weak acid.

$$K_a = x^2/I$$

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

$$x = [H^+] = 1.6 \times 10^{-3} M$$

$$pH = -\log [H^+] = -\log (1.6 \times 10^{-3}) = 2.78$$

Calculations Involving Weak Bases

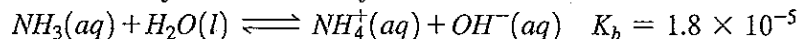
Like weak acids, all weak bases have the same ICE table. Even better, the ICE table for weak bases is the same as that for weak acids, except that base ionization produces hydroxide ion rather than hydrogen ion.

Example:

* Calculate the pH of a 0.75 M solution of aqueous ammonia.

Solution:

Set up an ICE table for the reaction of ammonia with water:



I	I	0	0
C	-y	+y	+y
E	I-y	y	y

For clarity, "y" is used instead of "x" to represent the number of moles per liter of base that ionizes.

$$K_b = [OH^-][NH_4^+]/[NH_3] = (y)(y)/(I-y)$$

If $I > 100 K_b$, then y is very small compared to I , so the generic equation for calculations involving weak base ionizations is:

$$K_b = y^2/I$$

where K_b is the ionization constant for the weak base, y is the number of moles per liter of weak base that ionizes, and I is the initial molar concentration of weak base.

$$K_b = y^2/I$$

$$1.8 \times 10^{-5} = y^2/0.75$$

$$y = [OH^-] = 3.7 \times 10^{-3} M$$

$$pOH = -\log [OH^-] = -\log (3.7 \times 10^{-3}) = 2.43$$

$$pH = 14 - pOH = 14 - 2.43 = 11.57$$

Your Turn 16.6

Classify the following 0.10 M solutions as strong or weak acids or bases: hydrochloric acid, ammonium chloride, calcium hydroxide, ethylamine, and sodium cyanide. Estimate the approximate pH for each solution. Justify your answers.

Write your answers in the space provided.

- .10M HCl \rightarrow strong acid $\text{pH} = -\log [1.0] = 1$
 .10M $\text{NH}_4\text{Cl} \rightarrow$ weak acid $\text{pH} = \text{NH}_4^+ \rightarrow \text{NH}_3 + [\text{H}^+] = .001 \approx 3$
 .01M $\text{Ca}(\text{OH})_2 \rightarrow$ strong base, dibasic $\text{pH} \approx 12-13$
 .01M ethylamine \rightarrow weak base (amine) $\text{pH} \approx 7-9$
 .01M NaCN \rightarrow weak base of HCN $\text{pH} \approx 7-9$

Lowest pH \rightarrow Highest pH
 $\text{NaHSO}_4 < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaHCO}_3 < \text{Na}_2\text{CO}_3$
 acidic acidic neutral basic basic

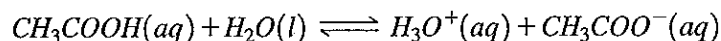
Once the identity of a strong or weak acid or base solution is established, the calculations fall into a predictable pattern.

Example:

- * Measurements show that the pH of a 0.10 M solution of acetic acid is 2.87.
 * Calculate K_b for potassium acetate, CH_3COOK . Find K_a then use it to calculate K_b

Solution:

The question provides information for a solution of a weak acid but asks for the K_b of its conjugate weak base. First, calculate K_a for the weak acid and then convert it to K_b for the conjugate base.



$$K_a = x^2/I$$

$$\text{If the pH is 2.87, the } [\text{H}^+] = 10^{-2.87} = 1.3 \times 10^{-3} \text{ M.}$$

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] = x = 1.3 \times 10^{-3} \text{ M}$$

Substituting:

$$K_a = x^2/(0.10 - x)$$

$$K_a = (1.3 \times 10^{-3})(1.3 \times 10^{-3})/(0.10 - 1.3 \times 10^{-3} \text{ M})$$

$$K_a = 1.7 \times 10^{-5}$$

$$K_b = K_w/K_a = 1.0 \times 10^{-14}/1.7 \times 10^{-5} = 5.9 \times 10^{-10}$$

Acid-Base Properties of Salt Solutions

Section 16.9

- * **Hydrolysis** of salts refers to the reactions of salt ions with water. Recall that, except for the anions of strong acids, anions tend to be weak bases. Their negative charges tend to attract protons from water. Similarly, except for the cations of strong bases,

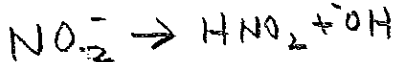
* cations are weakly acidic, either by attracting a pair of electrons from water, as with Lewis acids, or by donating an available proton to water.

* To classify a salt solution as acidic, basic, or neutral, disregard any neutral cations or anions listed in Table 16.2. If what is left is an anion, the salt is basic. If a cation remains, the salt is acidic. If both the cation and anion are listed in Table 16.2, the salt is neutral. If neither the cation nor anion is neutral, the acid or base character of the salt cannot be determined by examining its formula.

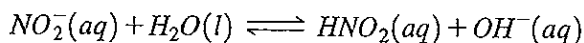
Example:

Classify the salt, sodium nitrite, NaNO_2 , as acid, base, or neutral. Explain your reasoning. Write a chemical equation for its reaction with water.

Solution:

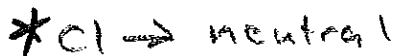


Sodium nitrite is a base. The sodium ion is a cation of a strong base, so it is neutral. Nitrite is the conjugate base of the weak acid, nitrous acid, HNO_2 . A solution of sodium nitrite in water will be basic because of the hydrolysis reaction of the nitrite ion with water. (We ignore the sodium ion because it is neutral.) The K_b of the nitrite ion can be calculated from the K_a of nitrous acid.



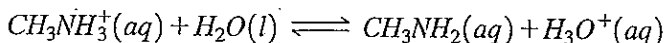
Example:

Classify an aqueous solution of methylammonium chloride, $\text{CH}_3\text{NH}_3\text{Cl}$, as acidic, basic, or neutral. Explain your reasoning. Write an equation to illustrate your answer.



Solution:

Methylammonium chloride is acidic because the chloride ion is neutral and the methylammonium ion is the conjugate weak acid of the base, methylamine, CH_3NH_2 . The K_a of methylammonium ion can be calculated from the K_b of methylamine.



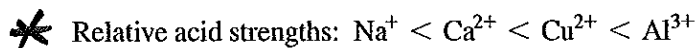
Section 16.10

Acid-Base Behavior and Chemical Structure

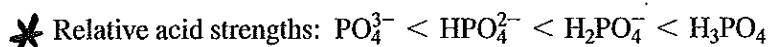
* Acidity of a substance is directly related to the strength of attraction for a pair of electrons to a central atom. Generally, acidity increases with stronger attractions for electrons.

Three factors affect attraction for electrons:

- * 1. **Ionic charge:** When comparing similar ions, the more positive ions are stronger acids. (The more negative ions are more strongly basic.) For example:



- * Metal cations of higher charge act as Lewis acids in water. The higher the charge, the greater the attraction for electrons and the stronger the acid. If the charges are equal, the smaller ion displays the stronger attraction for electrons.

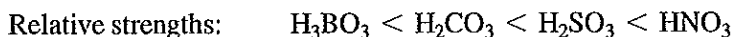


Note that, in this example, PO_4^{3-} is clearly a base because it has a negative charge, and H_3PO_4 is clearly an oxyacid. However, HPO_4^{2-} and H_2PO_4^- are recognized as amphoteric, because they are protonated anions. The ionic charge generalization cannot predict whether a substance will be an acid (more acidic than water) or a base (less acidic than water) relative to water. It can predict only the acidity of substances relative to each other.

- * 2. **Oxidation number:** When comparing similar formulas with the same central atom, the greater the oxidation number of the central atom, the stronger the acid. A greater number of electronegative oxygen atoms withdraws more electrons from the O—H bond, making the bond weaker. For example:



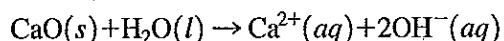
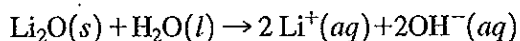
- * 3. **Electronegativity:** When comparing similar formulas with different central atoms, generally, the greater the electronegativity of the central atom, the stronger the acid.



(Recall that the electronegativity of elements generally increases from the lower left to the upper right of the periodic table.)

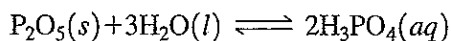
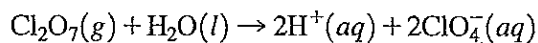
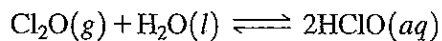
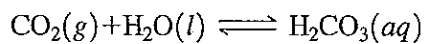
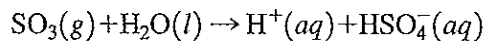
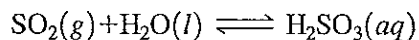
* Some Common Acid-Base Reactions

Strong bases also include oxides of Groups 1 and 2 such as Li_2O , MgO , and CaO . These "base anhydrides" react with water to give hydroxides:

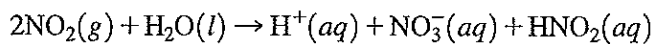


Metal Oxides

* Similarly, nonmetal oxides, called acid anhydrides, give solutions of acids in water.



* Notice that the nonmetal tends to retain its oxidation number when going from the oxide to the acid. One notable exception is the reaction of nitrogen dioxide with water to form nitric acid and nitrous acid.



Notice that in all the equations, whenever a strong acid is formed, it is written in its ionized form to reflect its strong electrolytic character.