

Chemistry, The Central Science, 10th edition
Theodore L. Brown; H. Eugene LeMay, Jr.;
and Bruce E. Bursten

Chapter 16

Acids and Bases

John D. Bookstaver
St. Charles Community College
St. Peters, MO
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Acids & Bases

- Acids: taste sour, litmus turns red
- Bases: taste bitter, litmus turns blue, feel slippery
- More H^+ than OH^- = acidic
- More OH^- than H^+ = basic
- When they react with each other; neutralization occurs



Some Definitions

- Arrhenius

- Acid: Substance that, when dissolved in water, increases the concentration of hydrogen ions.
- Base: Substance that, when dissolved in water, increases the concentration of hydroxide ions.



Some Definitions

- Brønsted–Lowry
 - Acid: Proton donor
 - Base: Proton acceptor



A Brønsted–Lowry acid...

...must have a removable (acidic) proton.

A Brønsted–Lowry base...

...must have a pair of nonbonding electrons.

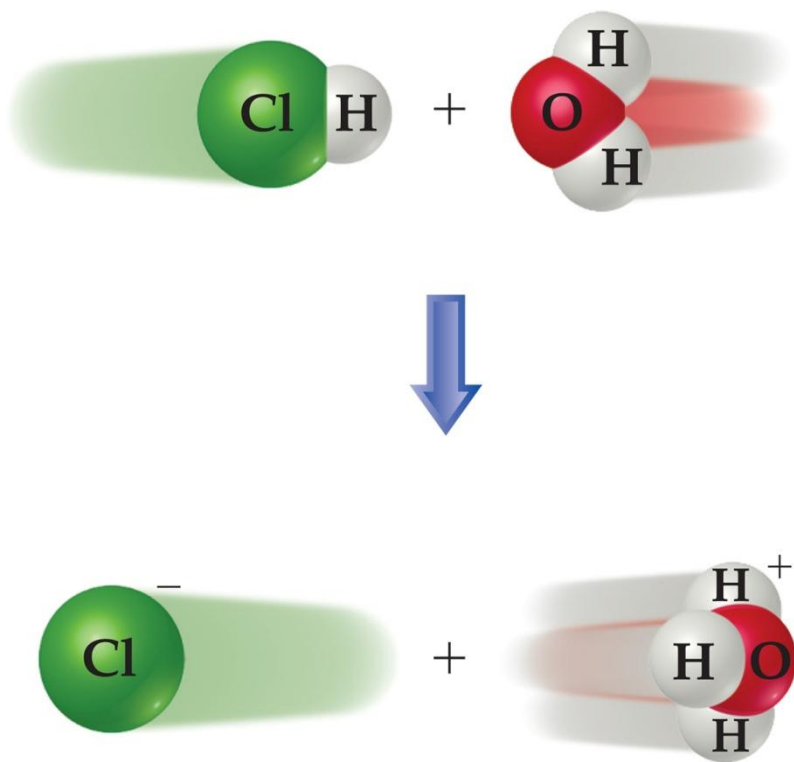


If it can be either...

...it is amphoteric.



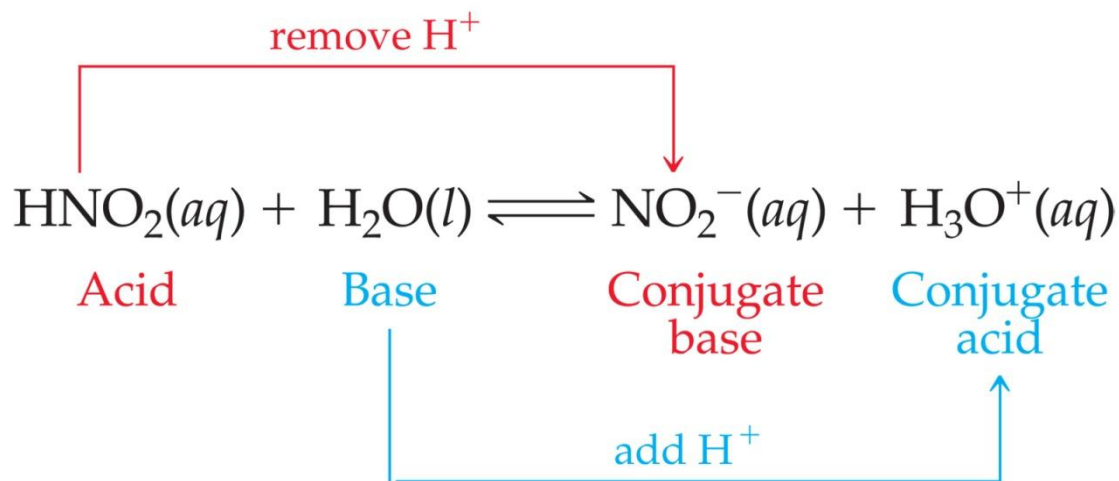
What Happens When an Acid Dissolves in Water?



- Water acts as a Brønsted–Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the conjugate base of the acid and a hydronium ion are formed.

Conjugate Acids and Bases:

- From the Latin word *conjugare*, meaning “to join together.”
- Reactions between acids and bases always yield their conjugate bases and acids.



SAMPLE EXERCISE 16.1 Identifying Conjugate Acids and Bases

(a) What is the conjugate base of each of the following acids: HClO_4 , H_2S , PH_4^+ , HCO_3^- ?

(b) What is the conjugate acid of each of the following bases: CN^- , SO_4^{2-} , H_2O , HCO_3^- ?

Solution

Analyze: We are asked to give the conjugate base for each of a series of species and to give the conjugate acid for each of another series of species.

Plan: The conjugate base of a substance is simply the parent substance minus one proton, and the conjugate acid of a substance is the parent substance plus one proton.

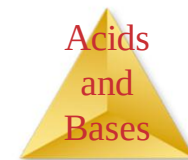
Solve: (a) HClO_4 less one proton (H^+) is ClO_4^- . The other conjugate bases are HS^- , PH_3 , and CO_3^{2-} . (b) CN^- plus one proton (H^+) is HCN . The other conjugate acids are HSO_4^- , H_3O^+ , and H_2CO_3 .

Notice that the hydrogen carbonate ion (HCO_3^-) is amphiprotic: It can act as either an acid or a base.

PRACTICE EXERCISE

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

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



SAMPLE EXERCISE 16.2 Writing Equations for Proton-Transfer Reactions

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

Solution

Analyze and Plan: We are asked to write two equations representing reactions between HSO_3^- and water, one in which HSO_3^- should donate a proton to water, thereby acting as a Brønsted–Lowry acid, and one in which HSO_3^- should accept a proton from water, thereby acting as a base. We are also asked to identify the conjugate pairs in each equation.

Solve: **(a)**



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

(b)



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

PRACTICE EXERCISE

When lithium oxide (Li_2O) is dissolved in water, the solution turns basic from the reaction of the oxide ion (O^{2-}) with water. Write the reaction that occurs, and identify the conjugate acid-base pairs.

Answer: $\text{O}^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{OH}^-(aq)$. OH^- is the conjugate acid of the base O^{2-} . OH^- is also the conjugate base of the acid H_2O .

Acids
and
Bases

Acid and Base Strength

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

- Strong acids are completely dissociated in water.
 - Their conjugate bases are quite weak.
- Weak acids only dissociate partially in water.
 - Their conjugate bases are weak bases.



Acid and Base Strength

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

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

Acid and Base Strength

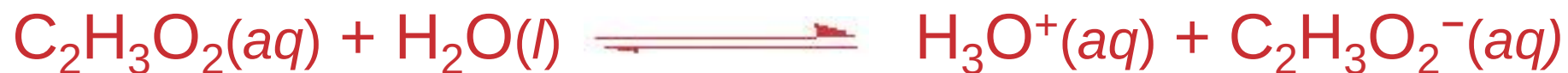
In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.



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



Acid and Base Strength



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



SAMPLE EXERCISE 16.3 Predicting the Position of a Proton-Transfer Equilibrium

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

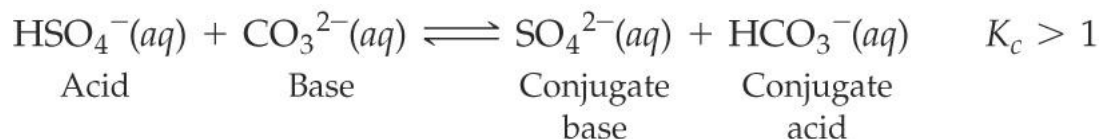


Solution

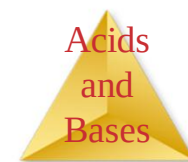
Analyze: We are asked to predict whether the equilibrium shown lies to the right, favoring products, or to the left, favoring reactants.

Plan: This is a proton-transfer reaction, and the position of the equilibrium will favor the proton going to the stronger of two bases. The two bases in the equation are CO_3^{2-} , the base in the forward reaction as written, and SO_4^{2-} , the conjugate base of HSO_4^- . We can find the relative positions of these two bases in [Figure 16.4](#) to determine which is the stronger base.

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



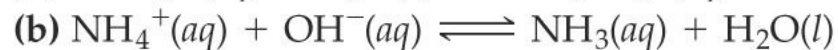
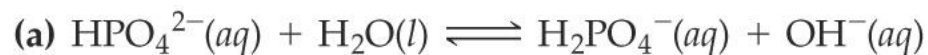
Comment: Of the two acids in the equation, HSO_4^- and HCO_3^- , the stronger one gives up a proton while the weaker one retains its proton. Thus, the equilibrium favors the direction in which the proton moves from the stronger acid and becomes bonded to the stronger base.



SAMPLE EXERCISE 16.3 continued

PRACTICE EXERCISE

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



Answers: (a) left, (b) right

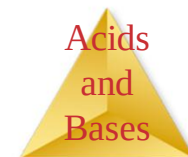


Autoionization of Water

- As we have seen, water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.



- This is referred to as **autoionization**.



Ion-Product Constant

- The equilibrium expression for this process is

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

- This special equilibrium constant is referred to as the **ion-product constant** for water, K_w .
- At 25°C, $K_w = 1.0 \times 10^{-14}$



SAMPLE EXERCISE 16.4 Calculating $[H^+]$ for Pure Water

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

Solution

Analyze: We are asked to determine the concentrations of hydronium and hydroxide ions in a neutral solution at 25°C .

Plan: We will use Equation 16.16 and the fact that, by definition, $[H^+] = [OH^-]$ in a neutral solution.

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

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

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7} \text{ M} = [H^+] = [OH^-]$$

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

PRACTICE EXERCISE

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

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

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



SAMPLE EXERCISE 16.5 Calculating $[H^+]$ from $[OH^-]$

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

Solution

Analyze: We are asked to calculate the hydronium ion concentration in an aqueous solution where the hydroxide concentration is known.

Plan: We can use the equilibrium-constant expression for the autoionization of water and the value of K_w to solve for each unknown concentration.

Solve: **(a)** Using Equation 16.16, we have:

$$\begin{aligned}[H^+][OH^-] &= 1.0 \times 10^{-14} \\ [H^+] &= \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12} \text{ M}\end{aligned}$$

This solution is basic because

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

(b) In this instance

$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6} \text{ M}$$

This solution is acidic because

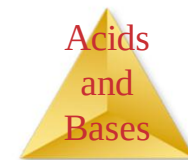
$$[H^+] > [OH^-]$$

SAMPLE EXERCISE 16.5 continued

PRACTICE EXERCISE

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

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



pH

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

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



pH

- In pure water,

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

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

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7}$$

pH

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

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

pH

These are the pH values for several common substances.



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

Acids
and
Bases

SAMPLE EXERCISE 16.6 Calculating pH from $[H^+]$

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

Solution

Analyze: We are asked to determine the pH of aqueous solutions for which we have already calculated $[H^+]$.

Plan: We can use the benchmarks in [Figure 16.5](#) to determine the pH for part (a) and to estimate pH for part (b). We can then use Equation 16.17 to calculate pH for part (b).

Solve: (a) In the first instance we found $[H^+]$ to be $1.0 \times 10^{-12} M$. Although we can use Equation 16.17 to determine the pH, 1.0×10^{-12} is one of the benchmarks in [Figure 16.5](#), so the pH can be determined without any formal calculation.

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

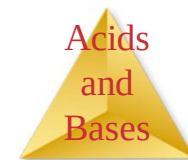
The rule for using significant figures with logs is that *the number of decimal places in the log equals the number of significant figures in the original number* (see Appendix A). Because 1.0×10^{-12} has two significant figures, the pH has two decimal places, 12.00.

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

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

Thus, we expect the pH to lie between 6.0 and 5.0. We use Equation 16.17 to calculate the pH.

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



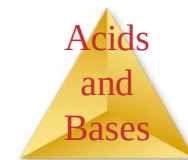
SAMPLE EXERCISE 16.6 continued

Check: After calculating a pH, it is useful to compare it to your prior estimate. In this case the pH, as we predicted, falls between 6 and 5. Had the calculated pH and the estimate not agreed, we should have reconsidered our calculation or estimate or both. Note that although $[\text{H}^+]$ lies halfway between the two benchmark concentrations, the calculated pH does not lie halfway between the two corresponding pH values. This is because the pH scale is logarithmic rather than linear.

PRACTICE EXERCISE

(a) In a sample of lemon juice $[\text{H}^+]$ is $3.8 \times 10^{-4} \text{ M}$. What is the pH? **(b)** A commonly available window-cleaning solution has a $[\text{H}^+]$ of $5.3 \times 10^{-9} \text{ M}$. What is the pH?

Answers: (a) 3.42, (b) 8.28



SAMPLE EXERCISE 16.7 Calculating $[H^+]$ from pH

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

Solution

Analyze: We need to calculate $[H^+]$ from pH.

Plan: We will use Equation 16.17, $pH = -\log [H^+]$, for the calculation.

Solve: From Equation 16.17, we have

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

Thus,

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

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

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

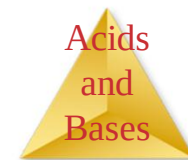
Comment: Consult the user's manual for your calculator to find out how to perform the antilog operation. The number of significant figures in $[H^+]$ is two because the number of decimal places in the pH is two.

Check: Because the pH is between 3.0 and 4.0, we know that $[H^+]$ will be between 1×10^{-3} and $1 \times 10^{-4} M$. Our calculated $[H^+]$ falls within this estimated range.

PRACTICE EXERCISE

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

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



SAMPLE EXERCISE 16.8 Calculating the pH of a Strong Acid

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

Solution

Analyze and Plan: We are asked to calculate the pH of a 0.040 *M* solution of HClO_4 . Because HClO_4 is a strong acid, it is completely ionized, giving $[\text{H}^+] = [\text{ClO}_4^-] = 0.040 \text{ M}$. Because $[\text{H}^+]$ lies between benchmarks 1×10^{-2} and 1×10^{-1} in [Figure 16.5](#), we estimate that the pH will be between 2.0 and 1.0.

Solve: The pH of the solution is given by

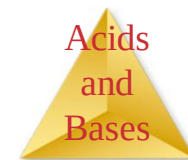
$$\text{pH} = -\log(0.040) = 1.40.$$

Check: Our calculated pH falls within the estimated range.

PRACTICE EXERCISE

An aqueous solution of HNO_3 has a pH of 2.34. What is the concentration of the acid?

Answer: 0.0046 *M*



Other “p” Scales

- The “p” in pH tells us to take the negative log of the quantity (in this case, hydrogen ions).
- Some similar examples are
 - $\text{pOH} = -\log [\text{OH}^-]$
 - $\text{p}K_w = -\log K_w$



Watch This!

Because

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

we know that

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

or, in other words,

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

SAMPLE EXERCISE 16.9 Calculating the pH of a Strong Base

What is the pH of **(a)** a 0.028 M solution of NaOH, **(b)** a 0.0011 M solution of Ca(OH)₂?

Solution

Analyze: We're asked to calculate the pH of two solutions, given the concentration of strong base for each.

Plan: We can calculate each pH by two equivalent methods. First, we could use Equation 16.16 to calculate [H⁺] and then use Equation 16.17 to calculate the pH. Alternatively, we could use [OH⁻] to calculate pOH and then use Equation 16.20 to calculate the pH.

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

Method 1:

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

Method 2:

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

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

Method 1:

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

Method 2:

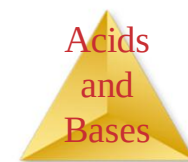
$$\text{pOH} = -\log(0.0022) = 2.66 \quad \text{pH} = 14.00 - \text{pOH} = 11.34$$

SAMPLE EXERCISE 16.9 continued

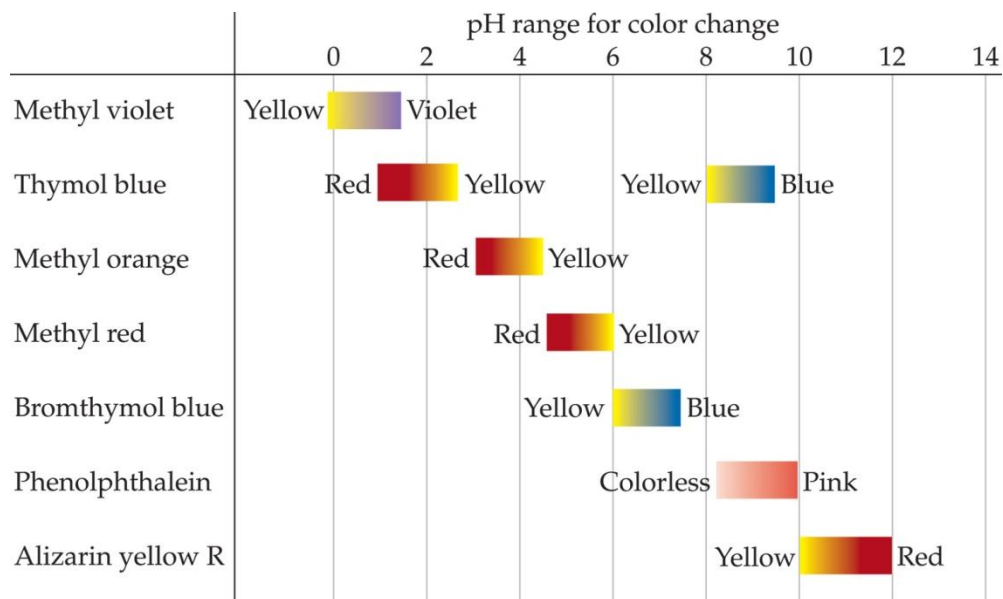
PRACTICE EXERCISE

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

Answers: **(a)** $7.8 \times 10^{-3} \text{ M}$, **(b)** $2.4 \times 10^{-13} \text{ M}$



How Do We Measure pH?



- For less accurate measurements, one can use
 - Litmus paper
 - “Red” paper turns blue above $\sim \text{pH} = 8$
 - “Blue” paper turns red below $\sim \text{pH} = 5$
 - An indicator

How Do We Measure pH?

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



Strong Acids

- You will recall that the seven strong acids are HCl, HBr, HI, HNO_3 , H_2SO_4 , HClO_3 , and HClO_4 .
- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.
- For the monoprotic strong acids,
$$[\text{H}_3\text{O}^+] = [\text{acid}].$$



Strong Bases

- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca^{2+} , Sr^{2+} , and Ba^{2+}).
- Again, these substances dissociate completely in aqueous solution.

Dissociation Constants

- For a generalized acid dissociation,



the equilibrium expression would be

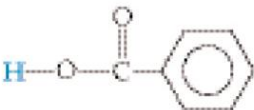
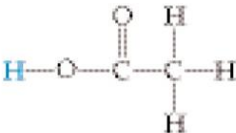
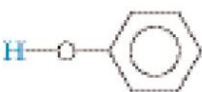
$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

- This equilibrium constant is called the acid-dissociation constant, K_a .



Dissociation Constants

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

Acid	Structural Formula	Conjugate Base	Equilibrium Reaction	K_a
Hydrofluoric (HF)		F^-	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	6.8×10^{-4}
Nitrous (HNO_2)		NO_2^-	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
Benzoic ($HC_7H_5O_2$)		$C_7H_5O_2^-$	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.3×10^{-5}
Acetic ($HC_2H_3O_2$)		$C_2H_3O_2^-$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous (HClO)		ClO^-	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	3.0×10^{-8}
Hydrocyanic (HCN)		CN^-	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol (HC_6H_5O)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

*The proton that ionizes is shown in blue.

Acids
and
Bases

Calculating K_a from the pH

- The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.
- We know that

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{COO}^-]}{[\text{HCOOH}]}$$

Calculating K_a from the pH

- The pH of a 0.10 M solution of formic acid, HCOOH , at 25°C is 2.38. Calculate K_a for formic acid at this temperature.
- To calculate K_a , we need the equilibrium concentrations of all three things.
- We can find $[\text{H}_3\text{O}^+]$, which is the same as $[\text{HCOO}^-]$, from the pH.



Calculating K_a from the pH

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

$$2.38 = -\log [\text{H}_3\text{O}^+]$$

$$-2.38 = \log [\text{H}_3\text{O}^+]$$

$$10^{-2.38} = 10^{\log [\text{H}_3\text{O}^+]} = [\text{H}_3\text{O}^+]$$

$$4.2 \times 10^{-3} = [\text{H}_3\text{O}^+] = [\text{HCOO}^-]$$



Calculating K_a from pH

Now we can set up a table...

	[HCOOH], M	[H ₃ O ⁺], M	[HCOO ⁻], M
Initially	0.10	0	0
Change	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
At Equilibrium	$0.10 - 4.2 \times 10^{-3}$ $= 0.0958 = 0.10$	4.2×10^{-3}	4.2×10^{-3}

Calculating K_a from pH

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

Calculating Percent Ionization

- Percent Ionization = $\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_{\text{initial}}} \times 100$

- In this example

$$[\text{H}_3\text{O}^+]_{\text{eq}} = 4.2 \times 10^{-3} \text{ M}$$

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

Calculating Percent Ionization

$$\begin{aligned}\text{Percent Ionization} &= \frac{4.2 \times 10^{-3}}{0.10} \times 100 \\ &= 4.2\%\end{aligned}$$



SAMPLE EXERCISE 16.10 Calculating K_a and Percent Ionization from Measured pH

A student prepared a 0.10 M solution of formic acid (HCHO_2) and measured its pH using a pH meter of the type illustrated in [Figure 16.6](#). The pH at 25°C was found to be 2.38. **(a)** Calculate K_a for formic acid at this temperature. **(b)** What percentage of the acid is ionized in this 0.10 M solution?

Solution

Analyze: We are given the molar concentration of an aqueous solution of weak acid and the pH of the solution at 25°C, and we are asked to determine the value of K_a for the acid and the percentage of the acid that is ionized.

Plan: Although we are dealing specifically with the ionization of a weak acid, this problem is very similar to the equilibrium problems we encountered in Chapter 15. We can solve it using the method first outlined in Sample Exercise 15.8, starting with the chemical reaction and a tabulation of initial and equilibrium concentrations.

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



The equilibrium-constant expression is

$$K_a = \frac{[\text{H}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]}$$

From the measured pH, we can calculate $[\text{H}^+]$:

$$\begin{aligned}\text{pH} &= -\log[\text{H}^+] = 2.38 \\ \log[\text{H}^+] &= -2.38 \\ [\text{H}^+] &= 10^{-2.38} = 4.2 \times 10^{-3} M\end{aligned}$$

SAMPLE EXERCISE 16.10 continued

We can do a little accounting to determine the concentrations of the species involved in the equilibrium. We imagine that the solution is initially 0.10 M in HCHO_2 molecules. We then consider the ionization of the acid into H^+ and CHO_2^- . For each HCHO_2 molecule that ionizes, one H^+ ion and one CHO_2^- ion are produced in solution. Because the pH measurement indicates that $[\text{H}^+] = 4.2 \times 10^{-3}\text{ M}$ at equilibrium, we can construct the following table:

	$\text{HCHO}_2(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CHO}_2^-(aq)$
Initial	0.10 M		0		0
Change	$-4.2 \times 10^{-3}\text{ M}$		$+4.2 \times 10^{-3}\text{ M}$		$+4.2 \times 10^{-3}\text{ M}$
Equilibrium	$(0.10 - 4.2 \times 10^{-3})\text{ M}$		$4.2 \times 10^{-3}\text{ M}$		$4.2 \times 10^{-3}\text{ M}$

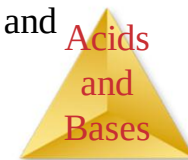
Notice that we have neglected the very small concentration of $\text{H}^+(aq)$ that is due to the autoionization of H_2O . Notice also that the amount of HCHO_2 that ionizes is very small compared with the initial concentration of the acid. To the number of significant figures we are using, the subtraction yields 0.10 M :

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

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

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

Check: The magnitude of our answer is reasonable because K_a for a weak acid is usually between 10^{-3} and 10^{-10} .



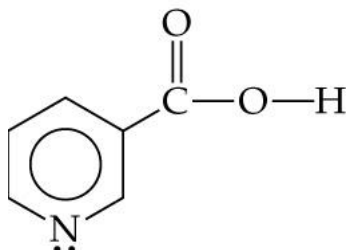
SAMPLE EXERCISE 16.10 continued

(b) The percentage of acid that ionizes is given by the concentration of H^+ or CHO_2^- at equilibrium, divided by the initial acid concentration, multiplied by 100%.

$$\text{Percent ionization} = \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HCHO}_2]_{\text{initial}}} \times 100\% = \frac{4.2 \times 10^{-3}}{0.10} \times 100\% = 4.2\%$$

PRACTICE EXERCISE

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



A 0.020 *M* solution of niacin has a pH of 3.26. **(a)** What percentage of the acid is ionized in this solution?

(b) What is the acid-dissociation constant, K_a , for niacin?

Answers: **(a)** 2.7%, **(b)** 1.5×10^{-5}

Calculating pH from K_a

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



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



Calculating pH from K_a

The equilibrium constant expression is

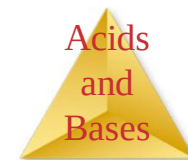
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Calculating pH from K_a

We next set up a table...

	$[\text{C}_2\text{H}_3\text{O}_2], M$	$[\text{H}_3\text{O}^+], M$	$[\text{C}_2\text{H}_3\text{O}_2^-], M$
Initially	0.30	0	0
Change	$-x$	$+x$	$+x$
At Equilibrium	$0.30 - x \approx 0.30$	x	x

We are assuming that x will be very small compared to 0.30 and can, therefore, be ignored.



Calculating pH from K_a

Now,

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

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

$$5.4 \times 10^{-6} = x^2$$

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

Calculating pH from K_a

$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log (2.3 \times 10^{-3}) \\ &= 2.64\end{aligned}$$

SAMPLE EXERCISE 16.11 Using K_a to Calculate pH

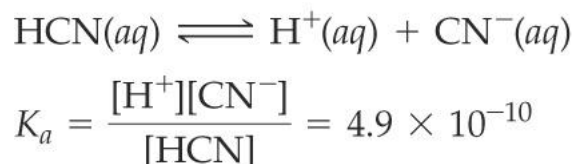
Calculate the pH of a 0.20 M solution of HCN. (Refer to [Table 16.2](#) or Appendix D for the value of K_a .)

Solution

Analyze: We are given the molarity of a weak acid and are asked for the pH. From [Table 16.2](#), K_a for HCN is 4.9×10^{-10} .

Plan: We proceed as in the example just worked in the text, writing the chemical equation and constructing a table of initial and equilibrium concentrations in which the equilibrium concentration of H^+ is our unknown.

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



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

	$\text{HCN}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CN}^-(aq)$
Initial	0.20 M		0		0
Change	$-x$ M		$+x$ M		$+x$ M
Equilibrium	$(0.20 - x)$ M		x M		x M

SAMPLE EXERCISE 16.11 continued

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

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

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

$$0.20 - x \cong 0.20$$

Thus

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

Solving for x , we have

$$\begin{aligned} x^2 &= (0.20)(4.9 \times 10^{-10}) = 0.98 \times 10^{-10} \\ x &= \sqrt{0.98 \times 10^{-10}} = 9.9 \times 10^{-6} \text{ M} = [\text{H}^+] \end{aligned}$$

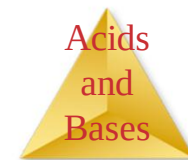
A concentration of $9.9 \times 10^{-6} \text{ M}$ is much smaller than 5% of 0.20, the initial HCN concentration. Our simplifying approximation is therefore appropriate. We now calculate the pH of the solution:

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

PRACTICE EXERCISE

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

Answer: 3.42



SAMPLE EXERCISE 16.12 Using K_a to Calculate Percent Ionization

Calculate the percentage of HF molecules ionized in **(a)** a 0.10 M HF solution, **(b)** a 0.010 M HF solution.

Solution

Analyze: We are asked to calculate the percent ionization of two HF solutions of different concentration.

Plan: We approach this problem as we would previous equilibrium problems. We begin by writing the chemical equation for the equilibrium and tabulating the known and unknown concentrations of all species. We then substitute the equilibrium concentrations into the equilibrium-constant expression and solve for the unknown concentration, that of H^+ .

Solve: **(a)** The equilibrium reaction and equilibrium concentrations are as follows:

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

The equilibrium-constant expression is

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

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

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

SAMPLE EXERCISE 16.12 continued

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

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

This equation can be solved using the standard quadratic formula.

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

Substituting the appropriate numbers gives

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

Of the two solutions, only the one that gives a positive value for *x* is chemically reasonable. Thus,

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

SAMPLE EXERCISE 16.12 continued

From our result, we can calculate the percent of molecules ionized:

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

(b) Proceeding similarly for the 0.010 M solution, we have

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

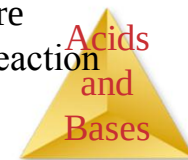
Solving the resultant quadratic expression, we obtain

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

The percentage of molecules ionized is

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

Comment: Notice that if we do not use the quadratic formula to solve the problem properly, we calculate 8.2% ionization for (a) and 26% ionization for (b). Notice also that in diluting the solution by a factor of 10, the percentage of molecules ionized increases by a factor of 3. This result is in accord with what we see in [Figure 16.9](#). It is also what we would expect from Le Châtelier's principle. • (Section 15.6) There are more “particles” or reaction components on the right side of the equation than on the left. Dilution causes the reaction to shift in the direction of the larger number of particles because this counters the effect of the decreasing concentration of particles.

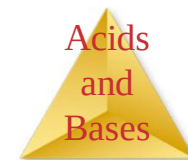


SAMPLE EXERCISE 16.12 continued

PRACTICE EXERCISE

In Practice Exercise 16.10, we found that the percent ionization of niacin ($K_a = 1.5 \times 10^{-5}$) in a 0.020 M solution is 2.7%. Calculate the percentage of niacin molecules ionized in a solution that is **(a)** 0.010 M , **(b)** $1.0 \times 10^{-3}\text{ M}$.

Answers: **(a)** 3.8%, **(b)** 12%



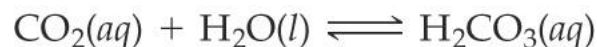
Polyprotic Acids

- Have more than one acidic proton.
- If the difference between the K_a for the first dissociation and subsequent K_a values is 10^3 or more, the pH generally depends *only* on the first dissociation.

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	1.0×10^{-3}	4.6×10^{-5}	

SAMPLE EXERCISE 16.13 Calculating the pH of a Polyprotic Acid Solution

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



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

Solution

Analyze: We are asked to determine the pH of a 0.0037 M solution of a polyprotic acid.

Plan: H_2CO_3 is a diprotic acid; the two acid-dissociation constants, K_{a1} and K_{a2} (Table 16.3), differ by more than a factor of 10^3 . Consequently, the pH can be determined by considering only K_{a1} , thereby treating the acid as if it were a monoprotic acid.

Solve: Proceeding as in Sample Exercises 16.11 and 16.12, we can write the equilibrium reaction and equilibrium concentrations as follows:

	$\text{H}_2\text{CO}_3(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{HCO}_3^-(aq)$
Initial	0.0037 M		0		0
Change	$-x\text{ M}$		$+x\text{ M}$		$+x\text{ M}$
Equilibrium	$(0.0037 - x)\text{ M}$		$x\text{ M}$		$x\text{ M}$

The equilibrium-constant expression is as follows:

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

SAMPLE EXERCISE 16.13 continued

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

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

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

$$0.0037 - x \simeq 0.0037$$

Thus,

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

Solving for x , we have

$$\begin{aligned} x^2 &= (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9} \\ x &= [\text{H}^+] = [\text{HCO}_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5} M \end{aligned}$$

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

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

Comment: If we were asked to solve for $[\text{CO}_3^{2-}]$, we would need to use K_{a2} . Let's illustrate that calculation. Using the values of $[\text{HCO}_3^-]$ and $[\text{H}^+]$ calculated above, and setting $[\text{CO}_3^{2-}] = y$, we have the following initial and equilibrium concentration values:

SAMPLE EXERCISE 16.13 continued



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

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

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

The value calculated for y is indeed very small compared to 4.0×10^{-5} , showing that our assumption was justified. It also shows that the ionization of HCO_3^- is negligible compared to that of H_2CO_3 , as far as production of H^+ is concerned. However, it is the *only* source of CO_3^{2-} , which has a very low concentration in the solution. Our calculations thus tell us that in a solution of carbon dioxide in water, most of the CO_2 is in the form of CO_2 or H_2CO_3 , a small fraction ionizes to form H^+ and HCO_3^- , and an even smaller fraction ionizes to give CO_3^{2-} . Notice also that $[\text{CO}_3^{2-}]$ is numerically equal to K_{a2} .

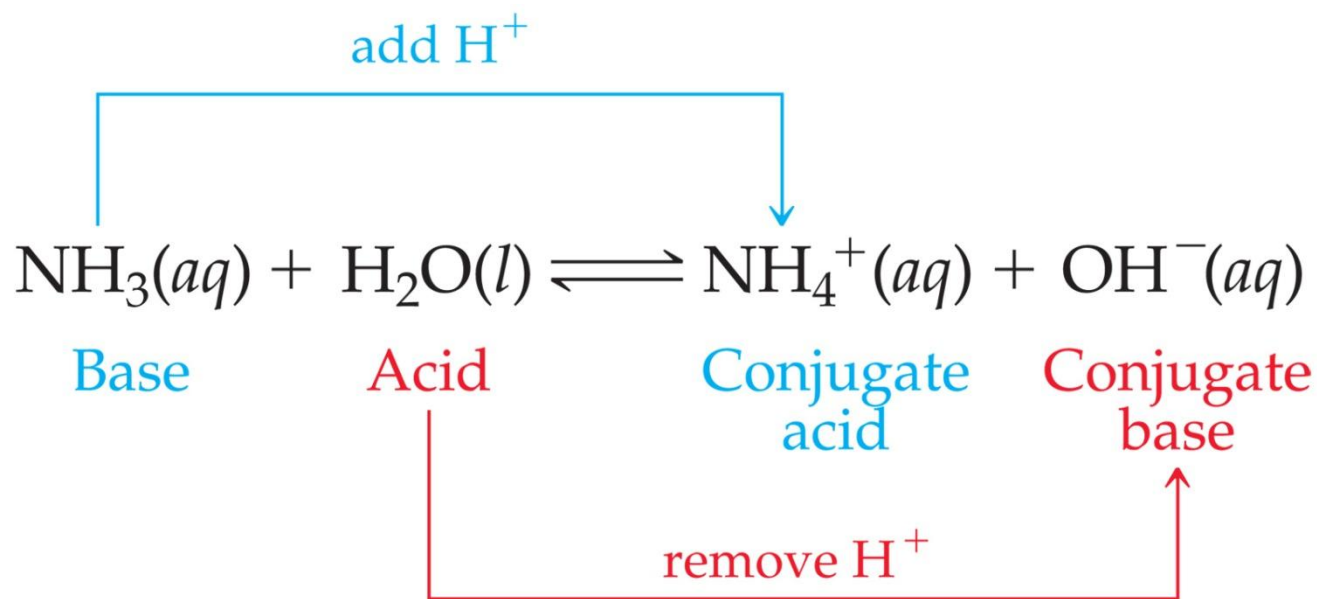
PRACTICE EXERCISE

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

Answers: (a) $\text{pH} = 1.80$, (b) $[\text{C}_2\text{O}_4^{2-}] = 6.4 \times 10^{-5} M$

Weak Bases

Bases react with water to produce hydroxide ion.



Weak Bases

The equilibrium constant expression for this reaction is

$$K_b = \frac{[\text{HB}] [\text{OH}^-]}{[\text{B}^-]}$$

where K_b is the base-dissociation constant.



SAMPLE EXERCISE 16.14 Using K_b to Calculate $[\text{OH}^-]$

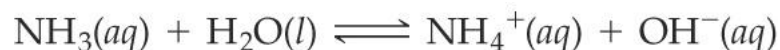
Calculate the concentration of OH^- in a 0.15 M solution of NH_3 .

Solution

Analyze: We are given the concentration of a weak base and are asked to determine the concentration of OH^- .

Plan: We will use essentially the same procedure here as used in solving problems involving the ionization of weak acids; that is, we write the chemical equation and tabulate initial and equilibrium concentrations.

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



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

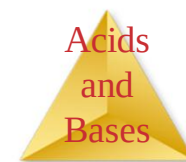
We then tabulate the equilibrium concentrations involved in the equilibrium:



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

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

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



SAMPLE EXERCISE 16.14 continued

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

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

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

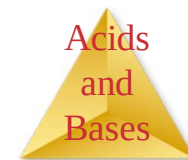
$$x = [\text{NH}_4^+] = [\text{OH}^-] = \sqrt{2.7 \times 10^{-6}} = 1.6 \times 10^{-3}\text{ M}$$

Check: The value obtained for x is only about 1% of the NH_3 concentration, 0.15 M . Therefore, neglecting x relative to 0.15 was justified.

PRACTICE EXERCISE

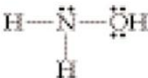
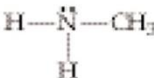
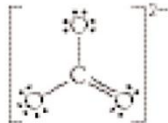
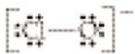
Which of the following compounds should produce the highest pH as a 0.05 M solution: pyridine, methylamine, or nitrous acid?

Answer: methylamine (because it has the largest K_b value)



Weak Bases

K_b can be used to find $[\text{OH}^-]$ and, through it, pH.

Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	K_b
Ammonia (NH_3)		NH_4^+	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}
Pyridine ($\text{C}_5\text{H}_5\text{N}$)		$\text{C}_5\text{H}_5\text{NH}^+$	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)		H_3NOH^+	$\text{H}_2\text{NOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{NOH}^+ + \text{OH}^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)		NH_3CH_3^+	$\text{NH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{CH}_3^+ + \text{OH}^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	$\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + \text{OH}^-$	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	$\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	$\text{ClO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{OH}^-$	3.3×10^{-7}

pH of Basic Solutions

What is the pH of a 0.15 M solution of NH_3 ?



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

pH of Basic Solutions

Tabulate the data.

Initially	0.15	0	0
At Equilibrium	$0.15 - x \approx 0.15$	x	x

pH of Basic Solutions

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

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

$$2.7 \times 10^{-6} = x^2$$

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



pH of Basic Solutions

Therefore,

$$[\text{OH}^-] = 1.6 \times 10^{-3} \text{ M}$$

$$\begin{aligned}\text{pOH} &= -\log (1.6 \times 10^{-3}) \\ &= 2.80\end{aligned}$$

$$\begin{aligned}\text{pH} &= 14.00 - 2.80 \\ &= 11.20\end{aligned}$$



SAMPLE EXERCISE 16.15 Using pH to Determine the Concentration of a Salt

A solution made by adding solid sodium hypochlorite (NaClO) to enough water to make 2.00 L of solution has a pH of 10.50. Using the information in Equation 16.37, calculate the number of moles of NaClO that were added to the water.

Solution

Analyze: We are given the pH of a 2.00-L solution of NaClO and must calculate the number of moles of NaClO needed to raise the pH to 10.50. NaClO is an ionic compound consisting of Na^+ and ClO^- ions. As such, it is a strong electrolyte that completely dissociates in solution into Na^+ , which is a spectator ion, and ClO^- ion, which is a weak base with $K_b = 3.33 \times 10^{-7}$ (Equation 16.37).

Plan: From the pH, we can determine the equilibrium concentration of OH^- . We can then construct a table of initial and equilibrium concentrations in which the initial concentration of ClO^- is our unknown. We can calculate $[\text{ClO}^-]$ using the equilibrium-constant expression, K_b .

Solve: We can calculate $[\text{OH}^-]$ by using either Equation 16.16 or Equation 16.19; we will use the latter method here:

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

$$[\text{OH}^-] = 10^{-3.50} = 3.16 \times 10^{-4} \text{ M}$$

This concentration is high enough that we can assume that Equation 16.37 is the only source of OH^- ; that is, we can neglect any OH^- produced by the autoionization of H_2O . We now assume a value of x for the initial concentration of ClO^- and solve the equilibrium problem in the usual way.



Initial	$x \text{ M}$	—	0	0
Change	$-3.16 \times 10^{-4} \text{ M}$	—	$+3.16 \times 10^{-4} \text{ M}$	$+3.16 \times 10^{-4} \text{ M}$
Final	$(x - 3.16 \times 10^{-4}) \text{ M}$	—	$3.16 \times 10^{-4} \text{ M}$	$3.16 \times 10^{-4} \text{ M}$

SAMPLE EXERCISE 16.15 continued

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

$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{(3.16 \times 10^{-4})^2}{x - 3.16 \times 10^{-4}} = 3.3 \times 10^{-7}$$

Thus

$$x = \frac{(3.16 \times 10^{-4})^2}{3.3 \times 10^{-7}} + (3.16 \times 10^{-4}) = 0.30 \text{ M}$$

We say that the solution is 0.30 M in NaClO, even though some of the ClO^- ions have reacted with water. Because the solution is 0.30 M in NaClO and the total volume of solution is 2.00 L, 0.60 mol of NaClO is the amount of the salt that was added to the water.

PRACTICE EXERCISE

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

Answer: 0.12 M

K_a and K_b

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

K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

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

SAMPLE EXERCISE 16.16 Calculating K_a or K_b for a Conjugate Acid-Base Pair

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

Solution

Analyze: We are asked to determine dissociation constants for F^- , the conjugate base of HF, and NH_4^+ , the conjugate acid of NH_3 .

Plan: Although neither F^- nor NH_4^+ appears in the tables, we can find the tabulated values for ionization constants for HF and NH_3 , and use the relationship between K_a and K_b to calculate the ionization constants for each of the conjugates.

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

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

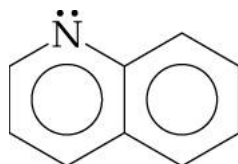
(b) K_b for NH_3 is listed in [Table 16.4](#) and in Appendix D as $K_b = 1.8 \times 10^{-5}$. Using Equation 16.40, we can calculate K_a for the conjugate acid, NH_4^+ :

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

SAMPLE EXERCISE 16.16 continued

PRACTICE EXERCISE

(a) Which of the following anions has the largest base-dissociation constant: NO_2^- , PO_4^{3-} , or N_3^- ? (b) The base quinoline has the following structure:



Its conjugate acid is listed in handbooks as having a $\text{p}K_a$ of 4.90. What is the base-dissociation constant for quinoline?

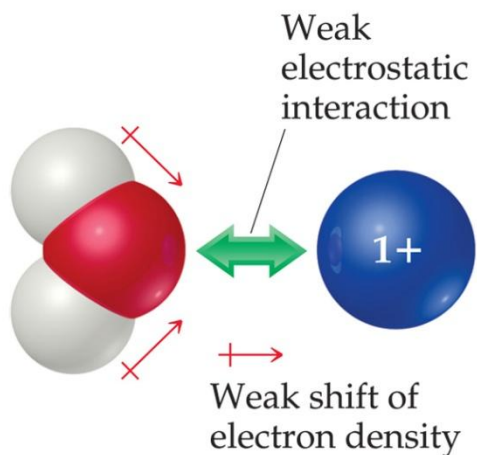
Answers: (a) PO_4^{3-} ($K_b = 2.4 \times 10^{-2}$), (b) 7.9×10^{-10}

Reactions of Anions with Water

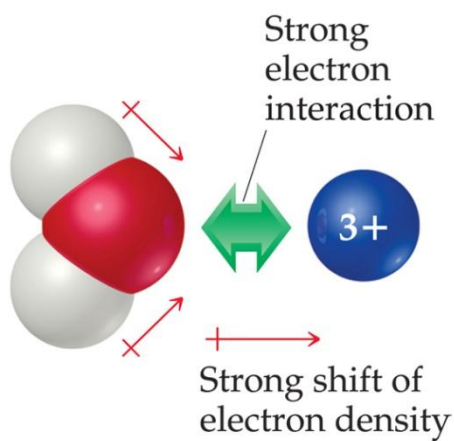
- Anions are bases.
- As such, they can react with water in a hydrolysis reaction to form OH^- and the conjugate acid:



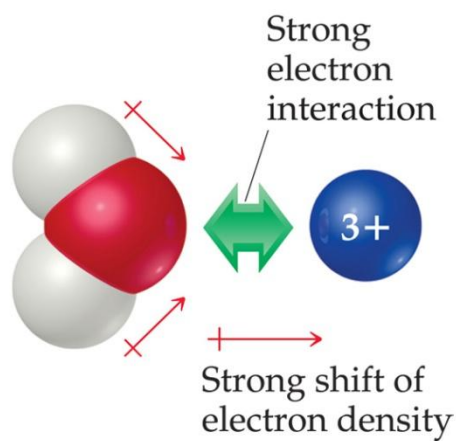
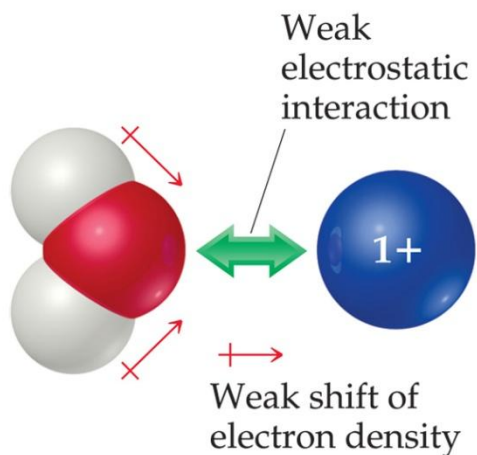
Reactions of Cations with Water



- Cations with acidic protons (like NH_4^+) will lower the pH of a solution.
- Most metal cations that are hydrated in solution also lower the pH of the solution.



Reactions of Cations with Water



- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O-H bond more polar and the water more acidic.
- Greater charge and smaller size make a cation more acidic.

Effect of Cations and Anions



1. An anion that is the conjugate base of a strong acid will not affect the pH.
2. An anion that is the conjugate base of a weak acid will increase the pH.
3. A cation that is the conjugate acid of a weak base will decrease the pH.

Salt:
Indicator:
Estimated pH:

NaNO_3	$\text{Ca}(\text{NO}_3)_2$	$\text{Zn}(\text{NO}_3)_2$	$\text{Al}(\text{NO}_3)_3$
Bromthymol blue	Bromthymol blue	Methyl red	Methyl orange
7.0	6.9	5.5	3.5

Effect of Cations and Anions

4. Cations of the strong Arrhenius bases will not affect the pH.
5. Other metal ions will cause a decrease in pH.
6. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the K_a and K_b values.



Salt:	NaNO_3	$\text{Ca}(\text{NO}_3)_2$	$\text{Zn}(\text{NO}_3)_2$	$\text{Al}(\text{NO}_3)_3$
Indicator:	Bromthymol blue	Bromthymol blue	Methyl red	Methyl orange
Estimated pH:	7.0	6.9	5.5	3.5

SAMPLE EXERCISE 16.17 Predicting the Relative Acidity of Salt Solutions

List the following solutions in order of increasing pH: (i) 0.1 M $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, (ii) 0.1 M NH_4Cl , (iii) 0.1 M $\text{NH}_3\text{CH}_3\text{Br}$, (iv) 0.1 M KNO_3 .

Solution

Analyze: We are asked to arrange a series of salt solutions in order of increasing pH (that is, from the most acidic to the most basic).

Plan: We can determine whether the pH of a solution is acidic, basic, or neutral by identifying the ions in solution and by assessing how each ion will affect the pH.

Solve: Solution (i) contains barium ions and acetate ions. Ba^{2+} is an ion of one of the heavy alkaline earth metals and will therefore not affect the pH (summary point 4). The anion, $\text{C}_2\text{H}_3\text{O}_2^-$, is the conjugate base of the weak acid $\text{HC}_2\text{H}_3\text{O}_2$ and will hydrolyze to produce OH^- ions, thereby making the solution basic (summary point 2). Solutions (ii) and (iii) both contain cations that are conjugate acids of weak bases and anions that are conjugate bases of strong acids. Both solutions will therefore be acidic. Solution (i) contains NH_4^+ , which is the conjugate acid of NH_3 ($K_b = 1.8 \times 10^{-5}$). Solution (iii) contains NH_3CH_3^+ , which is the conjugate acid of NH_2CH_3 ($K_b = 4.4 \times 10^{-4}$). Because NH_3 has the smaller K_b and is the weaker of the two bases, NH_4^+ will be the stronger of the two conjugate acids. Solution (ii) will therefore be the more acidic of the two. Solution (iv) contains the K^+ ion, which is the cation of the strong base KOH , and the NO_3^- ion, which is the conjugate base of the strong acid HNO_3 . Neither of the ions in solution (iv) will react with water to any appreciable extent, making the solution neutral. Thus, the order of pH is $0.1 \text{ M } \text{NH}_4\text{Cl} < 0.1 \text{ M } \text{NH}_3\text{CH}_3\text{Br} < 0.1 \text{ M } \text{KNO}_3 < 0.1 \text{ M } \text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$.

PRACTICE EXERCISE

In each of the following, indicate which salt will form the more acidic (or less basic) 0.010 M solution:

(a) NaNO_3 , $\text{Fe}(\text{NO}_3)_3$; (b) KBr , KBrO ; (c) $\text{CH}_3\text{NH}_3\text{Cl}$, BaCl_2 , (d) NH_4NO_2 , NH_4NO_3 .

Answers: (a) $\text{Fe}(\text{NO}_3)_3$, (b) KBr , (c) $\text{CH}_3\text{NH}_3\text{Cl}$, (d) NH_4NO_3



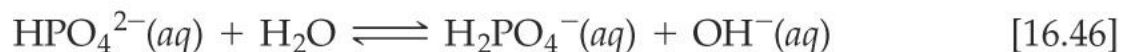
SAMPLE EXERCISE 16.18 Predicting Whether the Solution of an Amphiprotic Anion is Acidic or Basic

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

Solution

Analyze: We are asked to predict whether a solution of Na_2HPO_4 will be acidic or basic. This substance is an ionic compound composed of Na^+ and HPO_4^{2-} ions.

Plan: We need to evaluate each ion, predicting whether each is acidic or basic. Because Na^+ is the cation of a strong base, NaOH , we know that Na^+ has no influence on pH. It is merely a spectator ion in acid-base chemistry. Thus, our analysis of whether the solution is acidic or basic must focus on the behavior of the HPO_4^{2-} ion. We need to consider the fact that HPO_4^{2-} can act as either an acid or a base.



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

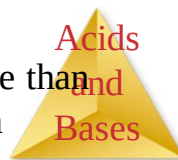
Solve: The value of K_a for Equation 16.45, as shown in [Table 16.3](#), is 4.2×10^{-13} . We must calculate the value of K_b for Equation 16.46 from the value of K_a for its conjugate acid, H_2PO_4^- . We make use of the relationship shown in Equation 16.40.

$$K_a \times K_b = K_w$$

We want to know K_b for the base HPO_4^{2-} , knowing the value of K_a for the conjugate acid H_2PO_4^- :

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

Because K_a for H_2PO_4^- is 6.2×10^{-8} ([Table 16.3](#)), we calculate K_b for HPO_4^{2-} to be 1.6×10^{-7} . This is more than 10^5 times larger than K_a for HPO_4^{2-} ; thus, the reaction shown in Equation 16.46 predominates over that in Equation 16.45, and the solution will be basic.



SAMPLE EXERCISE 16.18 continued

PRACTICE EXERCISE

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

Answer: acidic



Factors Affecting Acid Strength

	GROUP			
	4A	5A	6A	7A
Period 2	CH ₄ No acid or base properties	NH ₃ Weak base	H ₂ O ---	HF Weak acid
Period 3	SiH ₄ No acid or base properties	PH ₃ Weak base	H ₂ S Weak acid	HCl Strong acid

Increasing acid strength (vertical arrow pointing down)

Increasing base strength (vertical arrow pointing up)

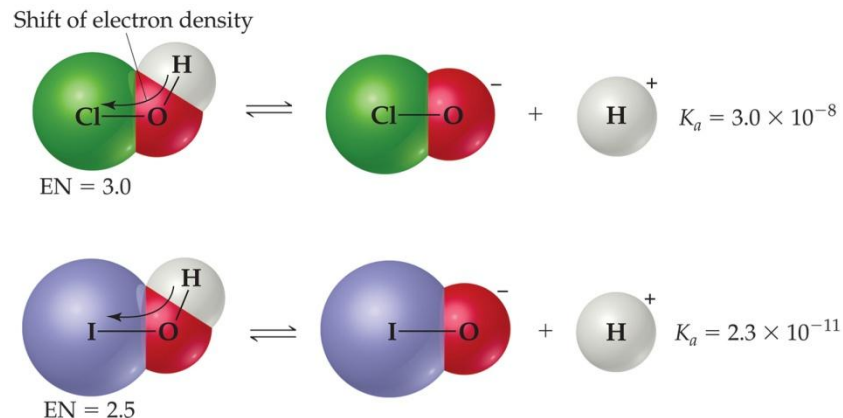
Increasing acid strength (horizontal arrow pointing right)

Increasing base strength (horizontal arrow pointing left)

- The more polar the H-X bond and/or the weaker the H-X bond, the more acidic the compound.
- Acidity increases from left to right across a row and from top to bottom down a group.

Factors Affecting Acid Strength

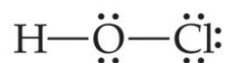
In oxyacids, in which an OH is bonded to another atom, Y, the more electronegative Y is, the more acidic the acid.



Acid	EN of Y	K_a
HClO	3.0	3.0×10^{-8}
HBrO	2.8	2.5×10^{-9}
HIO	2.5	2.3×10^{-11}

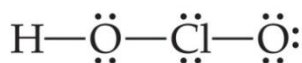
Factors Affecting Acid Strength

Hypochlorous



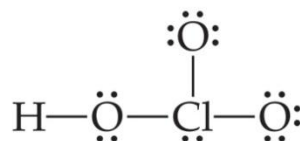
$$K_a = 3.0 \times 10^{-8}$$

Chlorous



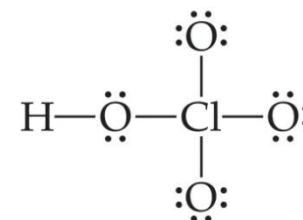
$$K_a = 1.1 \times 10^{-2}$$

Chloric



Strong acid

Perchloric



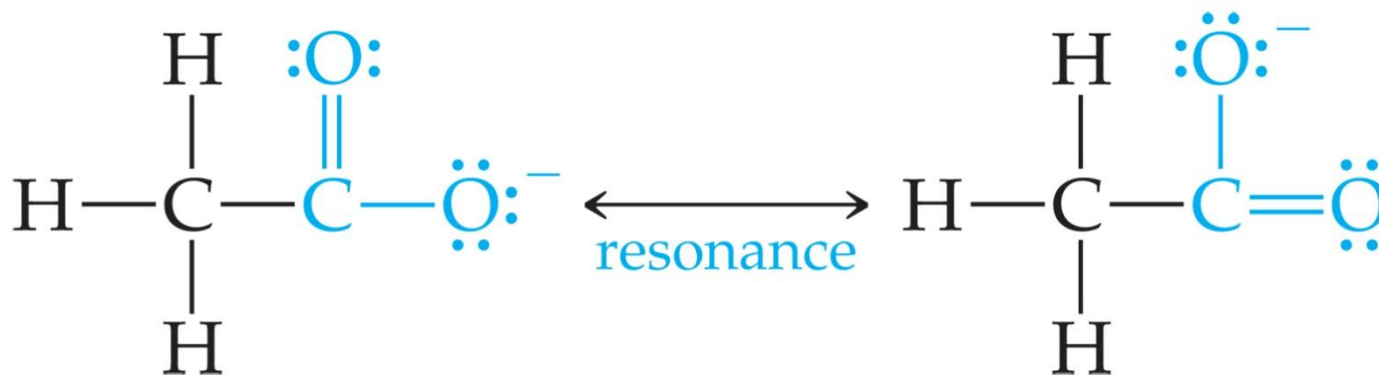
Strong acid


Increasing acid strength

For a series of oxyacids, acidity increases with the number of oxygens.

Factors Affecting Acid Strength

Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.



SAMPLE EXERCISE 16.19 Predicting Relative Acidities from Composition and Structure

Arrange the compounds in each of the following series in order of increasing acid strength: **(a)** AsH_3 , HI , NaH , H_2O ; **(b)** H_2SeO_3 , H_2SeO_4 , H_2O .

Solution

Analyze: We are asked to arrange two sets of compounds in order from weakest acid to strongest acid.

Plan: For the binary acids in part (a), we will consider the electronegativities of As, I, Na, and O, respectively. For the oxyacids in part (b), we will consider the number of oxygen atoms bonded to the central atom and the similarities between the Se-containing compounds and some more familiar acids.

Solve: **(a)** The elements from the left side of the periodic table form the most basic binary hydrogen compounds because the hydrogen in these compounds carries a negative charge. Thus NaH should be the most basic compound on the list. Because arsenic is less electronegative than oxygen, we might expect that AsH_3 would be a weak base toward water. That is also what we would predict by an extension of the trends shown in [Figure 16.13](#). Further, we expect that the binary hydrogen compounds of the halogens, as the most electronegative element in each period, will be acidic relative to water. In fact, HI is one of the strong acids in water. Thus the order of increasing acidity is $\text{NaH} < \text{AsH}_3 < \text{H}_2\text{O} < \text{HI}$.

(b) The acidity of oxyacids increases as the number of oxygen atoms bonded to the central atom increases. Thus, H_2SeO_4 will be a stronger acid than H_2SeO_3 ; in fact, the Se atom in H_2SeO_4 is in its maximum positive oxidation state, and so we expect it to be a comparatively strong acid, much like H_2SO_4 . H_2SeO_3 is an oxyacid of a nonmetal that is similar to H_2SO_3 . As such, we expect that H_2SeO_3 is able to donate a proton to H_2O , indicating that H_2SeO_3 is a stronger acid than H_2O . Thus, the order of increasing acidity is $\text{H}_2\text{O} < \text{H}_2\text{SeO}_3 < \text{H}_2\text{SeO}_4$.

PRACTICE EXERCISE

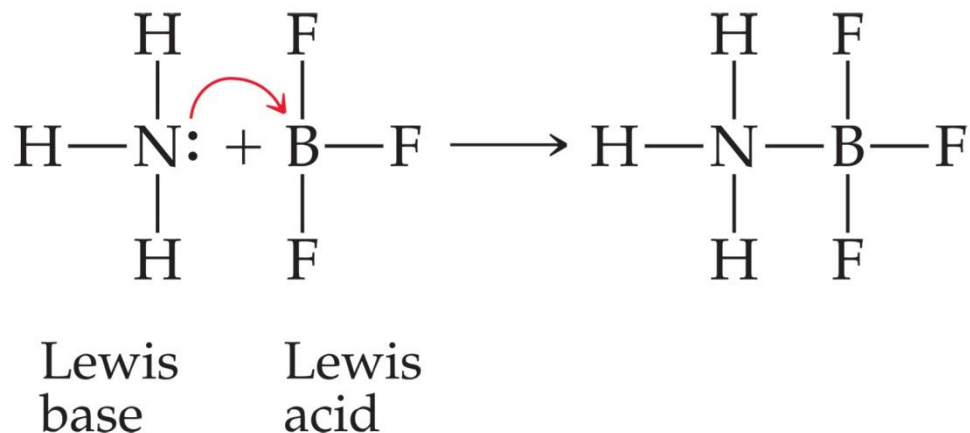
In each of the following pairs choose the compound that leads to the more acidic (or less basic) solution:

(a) HBr , HF ; **(b)** PH_3 , H_2S ; **(c)** HNO_2 , HNO_3 ; **(d)** H_2SO_3 , H_2SeO_3 .

Answers: **(a)** HBr , **(b)** H_2S , **(c)** HNO_3 , **(d)** H_2SO_3

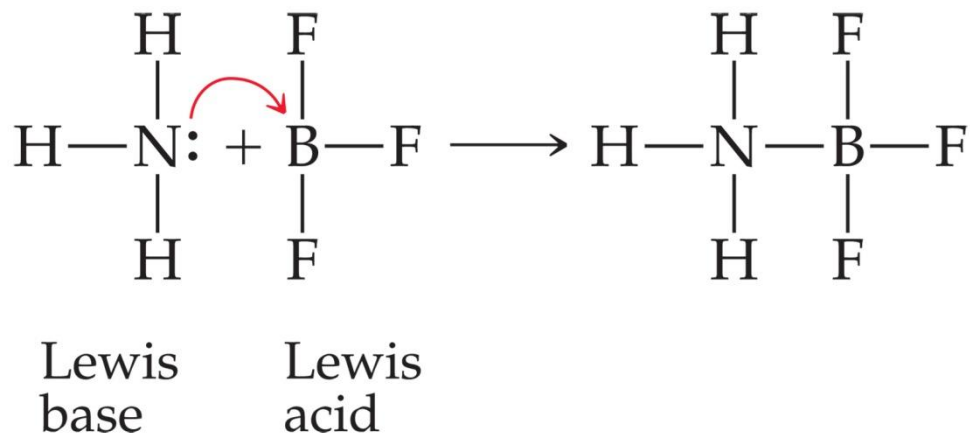


Lewis Acids



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.

Lewis Bases



- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted–Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.