

Weak Acids and Bases

The relative strengths of acids and bases are reflected in the magnitudes of their ionization constants; the stronger the acid or base, the larger its ionization constant. A reciprocal relation exists between the strengths of a conjugate acid-base pair: the stronger the acid, the weaker its conjugate base. Water exerts a leveling effect on dissolved acids or bases, reacting completely to generate its characteristic hydronium and hydroxide ions (the strongest acid and base that may exist in water).

23.1 Relative Strengths of Acids and Bases

Learning Objectives

By the end of this section, you will be able to:

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

23.2 Acid and Base Ionization Constants

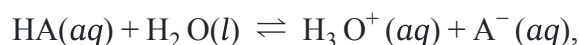
The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in [Figure 23.1](#).

Figure 23.1

Some of the common strong acids and bases are listed here.

6 Strong Acids		6 Strong Bases	
HClO ₄	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	Ca(OH) ₂	calcium hydroxide
HNO ₃	nitric acid	Sr(OH) ₂	strontium hydroxide
H ₂ SO ₄	sulfuric acid	Ba(OH) ₂	barium hydroxide

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a . For the reaction of an acid HA:



the acid ionization constant is written

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

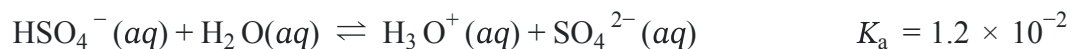
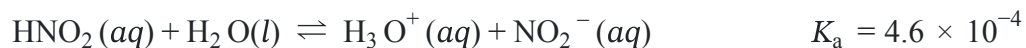
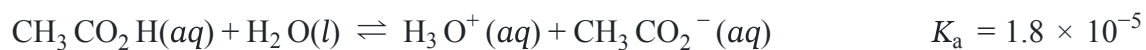
where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[\text{H}_2\text{O}]$ in the equation. The larger the K_a of an acid, the larger the concentration of



and A^- relative to the concentration of the nonionized acid, HA, in an equilibrium mixture, and the stronger the acid. An acid is classified as “strong” when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called “weak,” and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is provided in [Appendix H](#).

To illustrate this idea, three acid ionization equations and K_a values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order $\text{CH}_3\text{CO}_2\text{H} < \text{HNO}_2 <$





Another measure of the strength of an acid is its percent ionization. The percent ionization of a weak acid is defined in terms of the composition of an equilibrium mixture:

$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[\text{A}^-] = [\text{H}_3\text{O}^+]$). Unlike the K_a value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

EXAMPLE 23.2.1

Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HNO}_2]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[\text{H}_3\text{O}^+] = 10^{-2.09} = 0.0081\text{ M}$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

(Recall the provided pH value of 2.09 is logarithmic, and so it contains just two significant digits, limiting the certainty of the computed percent ionization.)

Check Your Learning

Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89.

✓ Answer

1.3% ionized

LINK TO LEARNING

View the [simulation](#) of strong and weak acids and bases at the molecular level.

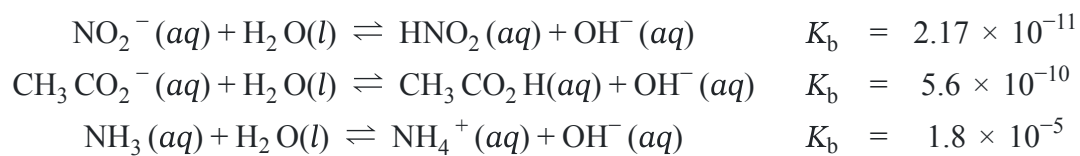
Just as for acids, the relative strength of a base is reflected in the magnitude of its base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:



the ionization constant is written as

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

Inspection of the data for three weak bases presented below shows the base strength increases in the order



A table of ionization constants for weak bases appears in [Appendix I](#). As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

$$\% \text{ ionization} = [OH^-]_{eq} / [B]_0 \times 100\%$$

but will vary depending on the base ionization constant and the initial concentration of the solution.

23.2.2 Calculating Percent Ionization

Percent Ionization
 0.100M HA, 1.23% ionized, what is the K_a


$$\begin{array}{rcl}
 \text{HA} + \text{H}_2\text{O} & \rightleftharpoons & \text{A}^- + \text{H}_3\text{O}^+ \\
 0.100 & & 0 \quad 0 \\
 -x & & +x \quad +x \\
 \hline
 0.100-x & & x
 \end{array}$$

1.23% of 0.100 = 0.00123M = x

$$K_a = \frac{x^2}{0.100-x} = \frac{(0.00123)^2}{(0.100-0.00123)}$$

$K_a = 1.53 \times 10^{-5}$

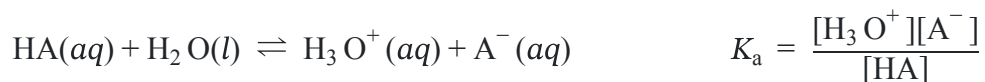
What is the pH?



[Watch on YouTube](#)

23.3 Relative Strengths of Conjugate Acid-Base Pairs

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, K_a or K_b , which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair HA / A^- , ionization equilibrium equations and ionization constant expressions are



Adding these two chemical equations yields the equation for the autoionization for water:



As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, K_w . By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$K_a = K_w / K_b \text{ or } K_b = K_w / K_a$$

The inverse proportional relation between K_a and K_b means *the stronger the acid or base, the weaker its conjugate partner*. [Figure 34.2](#) illustrates this relation for several conjugate acid-base pairs.

Figure 23.2

Relative strengths of several conjugate acid-base pairs are shown.

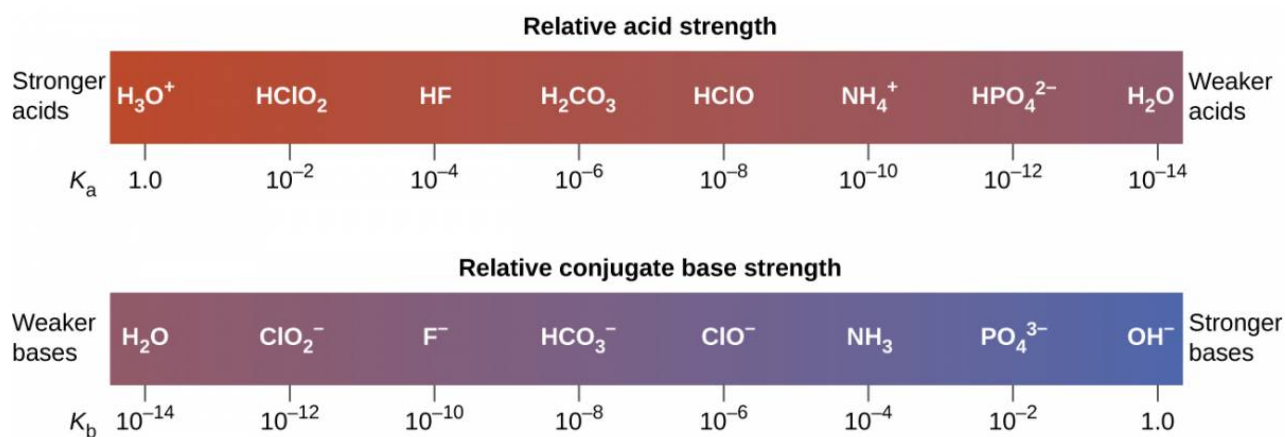


Figure 23.3

This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

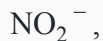
strong acid: $K_a \approx \infty$
conjugate base: $K_b = K_w / K_a = K_w / \infty \approx 0$

A similar approach can be used to support the observation that conjugate acids of strong bases ($K_b \approx \infty$) are of negligible strength ($K_a \approx 0$).

EXAMPLE 23.3.1

Calculating Ionization Constants for Conjugate Acid-Base Pairs

Use the K_b for the nitrite ion,



to calculate the K_a for its conjugate acid.

Solution

K_b for



is given in this section as 2.17

×

10^{-11} . The conjugate acid of



is HNO_2 ; K_a for HNO_2 can be calculated using the relationship:

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

Solving for K_a yields

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in [Appendix H](#).

Check Your Learning

Determine the relative acid strengths of



and HCN by comparing their ionization constants. The ionization constant of HCN is given in [Appendix H](#) as 4.9×10^{-10} . The ionization constant of



is not listed, but the ionization constant of its conjugate base, NH_3 , is listed as 1.8×10^{-5} .

✓ Answer



is the slightly stronger acid (K_a for



$$= 5.6$$

\times

$$10^{-10}).$$

23.4 Acid-Base Equilibrium Calculations

The chapter on chemical equilibria introduced several types of equilibrium calculations and the various mathematical strategies that are helpful in performing them. These strategies are generally useful for equilibrium systems regardless of chemical reaction class, and so they may be effectively applied to acid-base equilibrium problems. This section presents several example exercises involving equilibrium calculations for acid-base systems.





EXAMPLE 23.4.1

Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar ([Figure 23.4](#)) that provides its sour taste. At equilibrium, a solution contains $[\text{CH}_3\text{CO}_2\text{H}] = 0.0787\text{ M}$ and

$$[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CO}_2^-] = 0.00118\text{ M}.$$

What is the value of K_a for acetic acid?

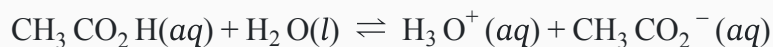
Figure 23.4

Vinegar contains acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)



Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_a for acetic acid.



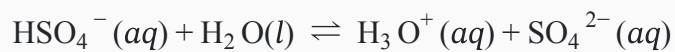
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Check Your Learning

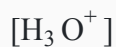
The



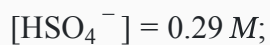
ion, weak acid used in some household cleansers:



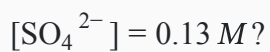
What is the acid ionization constant for this weak acid if an equilibrium mixture has the following composition:



= 0.027 M,



and



✓ Answer

K_a for



= 1.2

×

10^{-2}

EXAMPLE 23.4.2

Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050\text{ M}$,

$$[C_8H_{10}N_4O_2H^+]$$

$$= 5.0$$

×

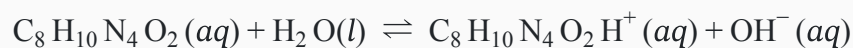
$$10^{-3}\text{ M}, \text{ and } [OH^-] = 2.5$$

×

$$10^{-3}\text{ M?}$$

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_b for caffeine.



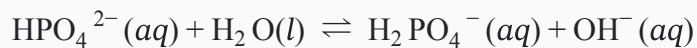
$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Check Your Learning

What is the equilibrium constant for the ionization of the



ion, a weak base



if the composition of an equilibrium mixture is as follows: $[OH^-] = 1.3$

×

$$10^{-6}\text{ M},$$

$$[H_2PO_4^-] = 0.042\text{ M};$$

and

$$[\text{HPO}_4^{2-}] = 0.341 \text{ M}?$$

✓ Answer

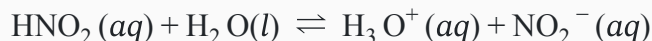
K_b for

$$\text{HPO}_4^{2-} = 1.6 \times 10^{-7}$$

EXAMPLE 23.4.3

Determination of K_a or K_b from pH

The pH of a 0.0516- M solution of nitrous acid, HNO_2 , is 2.34. What is its K_a ?



Solution

The nitrous acid concentration provided is a *formal* concentration, one that does not account for any chemical equilibria that may be established in solution. Such concentrations are treated as “initial” values for equilibrium calculations using the ICE table approach. Notice the initial value of hydronium ion is listed as *approximately* zero because a small concentration of H_3O^+ is present ($1 \times 10^{-7} M$) due to the autoprotolysis of water. In many cases, such as all the ones presented in this chapter, this concentration is much less than that generated by ionization of the acid (or base) in question and may be neglected.

The pH provided is a logarithmic measure of the hydronium ion concentration resulting from the acid ionization of the nitrous acid, and so it represents an “equilibrium” value for the ICE table:

$$[\text{H}_3\text{O}^+] = 10^{-2.34} = 0.0046 M$$

The ICE table for this system is then

	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$			
Initial concentration (M)	0.0516		~ 0	0
Change (M)	-0.0046		$+0.0046$	$+0.0046$
Equilibrium concentration (M)	0.0470		0.0046	0.0046

Finally, calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.6 \times 10^{-4}$$

Check Your Learning.

The pH of a solution of household ammonia, a 0.950- M solution of NH_3 , is 11.612. What is K_b for NH_3 .

✓ Answer

$$K_b = 1.8$$

×

10^{-5}

EXAMPLE 23.4.4

Calculating Equilibrium Concentrations in a Weak Acid Solution

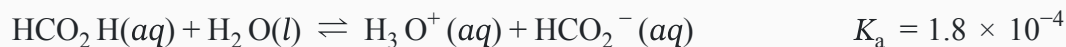
Formic acid, HCO_2H , is one irritant that causes the body's reaction to some ant bites and stings (Figure 23.5).

Figure 23.5

The pain of some ant bites and stings is caused by formic acid. (credit: John Tann)



What is the concentration of hydronium ion and the pH of a 0.534-M solution of formic acid?



Solution

The ICE table for this system is

	HCO_2H	+	H_2O	\rightleftharpoons	H_3O^+	+	HCO_2^-
Initial concentration (M)	0.534				~0		0
Change (M)					+x		+x
Equilibrium concentration (M)	0.534 - x				x		x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

The relatively large initial concentration and small equilibrium constant permits the simplifying assumption that x will be much lesser than 0.534, and so the equation becomes

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solving the equation for x yields

$$x^2 = 0.534 \times (1.8 \times 10^{-4}) = 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3} \text{ M}$$

To check the assumption that x is small compared to 0.534, its relative magnitude can be estimated:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2} \text{ (1.8\% of 0.534)}$$

Because x is less than 5% of the initial concentration, the assumption is valid.

As defined in the ICE table, x is equal to the equilibrium concentration of hydronium ion:

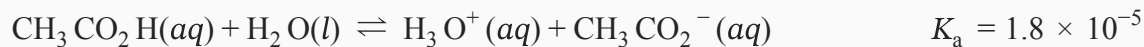
$$x = [\text{H}_3\text{O}^+] = 0.0098 \text{ M}$$

Finally, the pH is calculated to be

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0098) = 2.01$$

Check Your Learning

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of a 0.100- M solution of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$?



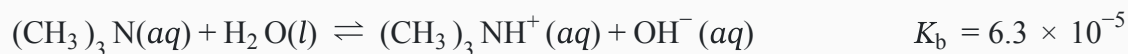
✓ Answer

percent ionization = 1.3%

EXAMPLE 23.4.5

Calculating Equilibrium Concentrations in a Weak Base Solution

Find the concentration of hydroxide ion, the pOH, and the pH of a 0.25-*M* solution of trimethylamine, a weak base:



Solution

The ICE table for this system is

	$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$			
Initial concentration (<i>M</i>)	0.25		0	~0
Change (<i>M</i>)	- <i>x</i>		<i>x</i>	<i>x</i>
Equilibrium concentration (<i>M</i>)	0.25 + (- <i>x</i>)		0 + <i>x</i>	~0 + <i>x</i>

Substituting the equilibrium concentration terms into the K_b expression gives

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

Assuming $x \ll 0.25$ and solving for x yields

$$x = 4.0 \times 10^{-3} \text{ M}$$

This value is less than 5% of the initial concentration (0.25), so the assumption is justified.

As defined in the ICE table, x is equal to the equilibrium concentration of hydroxide ion:

$$[\text{OH}^-] = \sim 0 + x = x = 4.0 \times 10^{-3} \text{ M}$$

$$= 4.0 \times 10^{-3} \text{ M}$$

The pOH is calculated to be

$$\text{pOH} = -\log(4.0 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{p}K_{\text{w}} = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

Check Your Learning

Calculate the hydroxide ion concentration and the percent ionization of a 0.0325-*M* solution of ammonia, a weak base with a K_{b} of 1.76×10^{-5} .

✓ Answer

7.56

×

10^{-4} M , 2.33%

In some cases, the strength of the weak acid or base and its formal (initial) concentration result in an appreciable ionization. Though the ICE strategy remains effective for these systems, the algebra is a bit more involved because the simplifying assumption that x is negligible cannot be made. Calculations of this sort are demonstrated in [Example 23.4.6](#) below.

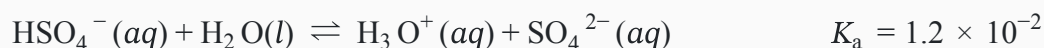
EXAMPLE 23.4.6

Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate, NaHSO_4 , is used in some household cleansers as a source of the



ion, a weak acid. What is the pH of a 0.50- M solution of



Solution

The ICE table for this system is

	HSO_4^-	$+$	H_2O	\rightleftharpoons	H_3O^+	$+$	SO_4^{2-}
Initial concentration (M)	0.50				~ 0		0
Change (M)	$-x$				$+x$		$+x$
Equilibrium concentration (M)	$0.50 - x$				x		x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.2 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If the assumption that $x \ll 0.5$ is made, simplifying and solving the above equation yields

$$x = 0.077 M$$

This value of x is clearly not significantly less than 0.50 M ; rather, it is approximately 15% of the initial concentration:

When we check the assumption, we calculate:

$$\frac{x}{[\text{HSO}_4^-]_i}$$

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15 \text{ (15\%)}$$

Because the simplifying assumption is not valid for this system, the equilibrium constant expression is solved as follows:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

Rearranging this equation yields

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^2$$

Writing the equation in quadratic form gives

$$x^2 + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

Solving for the two roots of this quadratic equation results in a negative value that may be discarded as physically irrelevant and a positive value equal to x . As defined in the ICE table, x is equal to the hydronium concentration.

$$x = [\text{H}_3\text{O}^+] = 0.072 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.072) = 1.14$$

Check Your Learning

Calculate the pH in a 0.010- M solution of caffeine, a weak base:



✓ Answer

pH 11.16

23.4.7 Calculating pH for a Solution of Weak Base

Handwritten notes for calculating the pH of a 0.15 M NH_3 solution. The notes include the base dissociation constant $K_b = 1.8 \times 10^{-5}$ and the equilibrium reaction:

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

An ICE table is shown:

R	NH_3	+	H_2O	\rightleftharpoons	NH_4^+	+	OH^-
I	0.15						
C	-x						
E	0.15 - x						

The equilibrium constant expression is given as:

$$K_b = [\text{NH}_4^+][\text{OH}^-]$$

A large red YouTube play button icon is overlaid on the notes. To the right of the notes is a small video thumbnail showing a person speaking.

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