

7.12: 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

Acid and Base Ionization Constants

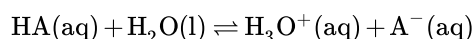
The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in Figure 7.12.1.

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

This table has seven rows and two columns. The first row is a header row, and it labels each column, “6 Strong Acids,” and, “6 Strong Bases.” Under the “6 Strong Acids” column are the following: H C l O subscript 4 perchloric acid; H C l hydrochloric acid; H B r hydrobromic acid; H I hydroiodic acid; H N O subscript 3 nitric acid; H subscript 2 S O subscript 4 sulfuric acid. Under the “6 Strong Bases” column are the following: L i O H lithium hydroxide; N a O H sodium hydroxide; K O H potassium hydroxide; C a (O H) subscript 2 calcium hydroxide; S r (O H) subscript 2 strontium hydroxide; B a (O H) subscript 2 barium hydroxide.

Figure 7.12.1: Some of the common strong acids and bases are listed here.

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

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

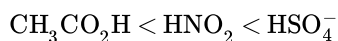
where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[\text{H}_2\text{O}]$ in the equation.

Note

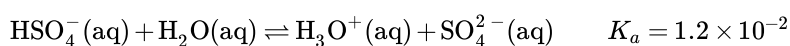
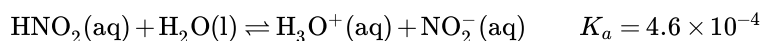
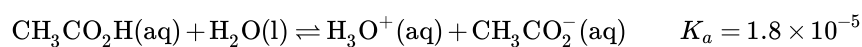
Equilibrium constant expressions are actually ratios of *activities*, and the value of K is determined at the limit of infinite dilution of the solutes. In these very dilute solutions, the activity of the solvent has a value of unity (1) and the activity of each solute can be approximated by its molar concentration.

The larger the K_a of an acid, the larger the concentration of H_3O^+ 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:



as demonstrated with the equations below:



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:

$$\% \text{ ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[A^-] = [H_3O^+]$). 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 7.12.1: 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:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[H_3O^+] = 10^{-2.09} = 0.0081M$$

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.)

? Exercise 7.12.1

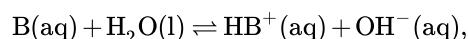
Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

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

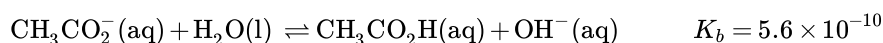
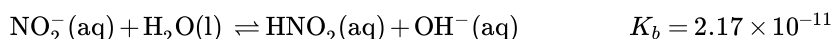
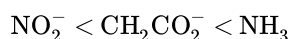
Just as for acids, the relative strength of a base is reflected in the magnitude of its base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger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



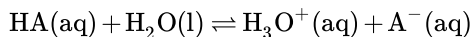
A table of ionization constants for weak bases appears in Appendix I. As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

$$\% \text{ ionization} = \left(\frac{[OH^-]_{eq}}{[B]_0} \right) \times 100\%$$

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

Relative Strengths of Conjugate Acid-Base Pairs

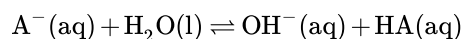
Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, K_a or K_b , which represents the extent of the acid or base ionization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



with

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

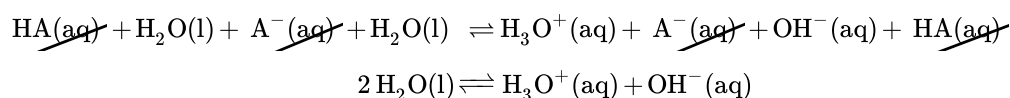
and



with

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

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

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

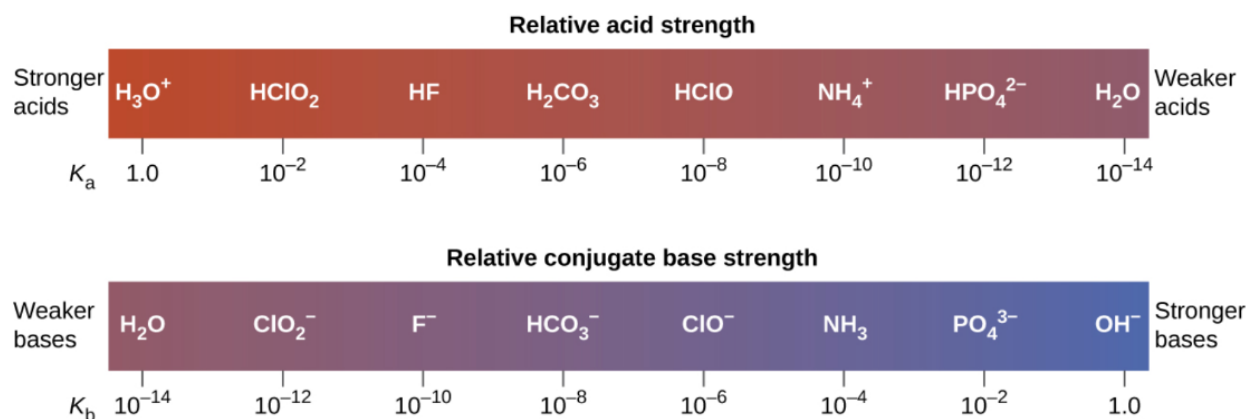
This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, K_w . By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$K_a = \frac{K_w}{K_b}$$

or

$$K_b = \frac{K_w}{K_a}$$

The inverse proportional relation between K_a and K_b means the stronger the acid or base, the weaker its **conjugate partner**. Figure 7.12.2 illustrates this relation for several conjugate acid-base pairs.





The diagram shows two horizontal bars. The first, labeled, “Relative acid strength,” at the top is red on the left and gradually changes to purple on the right. The red end at the left is labeled, “Stronger acids.” The purple end at the right is labeled, “Weaker acids.” Just outside the bar to the lower left is the label, “ K_a .” The bar is marked off in increments with a specific acid listed above each increment. The first mark is at 1.0 with H_3O^+ . The second is ten raised to the negative two with HClO_2 . The third is ten raised to the negative four with HF . The fourth is ten raised to the negative six with H_2CO_3 . The fifth is ten raised to a negative eight with HClO . The sixth is ten raised to the negative ten with NH_4^+ . The seventh is ten raised to a negative twelve with HPO_4^{2-} . The eighth is ten raised to the negative fourteen with H_2O . Similarly the second bar, which is labeled “Relative conjugate base strength,” is purple at the left end and gradually becomes blue at the right end. Outside the bar to the left is the label, “Weaker bases.” Outside the bar to the right is the label, “Stronger bases.” Below and to the left of the bar is the label, “ K_b .” The bar is similarly marked at increments with bases listed above each increment. The first is at ten raised to the negative fourteen with H_2O above it. The second is ten raised to the negative twelve with ClO_2^- above it. The third is ten raised to the negative ten with F^- above it. The fourth is ten raised to a negative eight with HCO_3^- above it. The fifth is ten raised to the negative six with ClO^- above it. The sixth is ten raised to the negative four with NH_3 above it. The seventh is ten raised to the negative two with PO_4^{3-} above it. The eighth is 1.0 with OH^- above it.

Figure 7.12.2 Relative strengths of several conjugate acid-base pairs are shown.

The listing of conjugate acid–base pairs shown in Figure 7.12.3 is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table’s columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not Bronsted-Lowry acids. All

the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, whereas those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

Acid			Base		
	perchloric acid	HClO_4	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
	sulfuric acid	H_2SO_4		HSO_4^-	hydrogen sulfate ion
	hydrogen iodide	HI		I^-	iodide ion
	hydrogen bromide	HBr		Br^-	bromide ion
	hydrogen chloride	HCl		Cl^-	chloride ion
	nitric acid	HNO_3	Undergo complete acid ionization in water	NO_3^-	nitrate ion
	hydronium ion	H_3O^+		H_2O	water
	hydrogen sulfate ion	HSO_4^-		SO_4^{2-}	sulfate ion
	phosphoric acid	H_3PO_4		H_2PO_4^-	dihydrogen phosphate ion
	hydrogen fluoride	HF		F^-	fluoride ion
	nitrous acid	HNO_2		NO_2^-	nitrite ion
	acetic acid	$\text{CH}_3\text{CO}_2\text{H}$		CH_3CO_2^-	acetate ion
	carbonic acid	H_2CO_3		HCO_3^-	hydrogen carbonate ion
	hydrogen sulfide	H_2S		HS^-	hydrogen sulfide ion
	ammonium ion	NH_4^+		NH_3	ammonia
	hydrogen cyanide	HCN		CN^-	cyanide ion
	hydrogen carbonate ion	HCO_3^-		CO_3^{2-}	carbonate ion
	water	H_2O		OH^-	hydroxide ion
	hydrogen sulfide ion	HS^-		S^{2-}	sulfide ion
	ethanol	$\text{C}_2\text{H}_5\text{OH}$		$\text{C}_2\text{H}_5\text{O}^-$	ethoxide ion
	ammonia	NH_3		NH_2^-	amide ion
	hydrogen	H_2		H^-	hydride ion
	methane	CH_4		CH_3^-	methide ion
					

This figure includes a table separated into a left half which is labeled “Acids” and a right half labeled “Bases.” A red arrow points up the left side, which is labeled “Increasing acid strength.” Similarly, a blue arrow points downward along the right side, which is labeled “Increasing base strength.” Names of acids and bases are listed next to each arrow toward the center of the table, followed by chemical formulas. Acids listed top to bottom are sulfuric acid, H_2SO_4 , hydrogen iodide, HI , hydrogen bromide, HBr , hydrogen chloride, HCl , nitric acid, HNO_3 , hydronium ion (in pink text) H_3O^+ , hydrogen sulfate ion, HSO_4^- , phosphoric acid, H_3PO_4 , hydrogen fluoride, HF , nitrous acid, HNO_2 , acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, carbonic acid H_2CO_3 , hydrogen sulfide, H_2S , ammonium ion, NH_4^+ , hydrogen cyanide, HCN , hydrogen carbonate ion, HCO_3^- , water (shaded in beige) H_2O , hydrogen sulfide ion, HS^- , ethanol, $\text{C}_2\text{H}_5\text{OH}$, ammonia, NH_3 , hydrogen, H_2 , methane, and CH_4 . The acids at the top of the listing from sulfuric acid through nitric acid are grouped with a bracket to the right labeled “Undergo complete acid ionization in water.” Similarly, the acids at the bottom from hydrogen sulfide ion through methane are grouped with a bracket and labeled, “Do not undergo acid ionization in water.” The right half of the figure lists bases and formulas. From top to bottom the bases listed are hydrogen sulfate ion, HSO_4^- , iodide ion, I^- , bromide ion, Br^- , chloride ion, Cl^- , nitrate ion, NO_3^- , water (shaded in beige), H_2O , sulfate ion, SO_4^{2-} , dihydrogen phosphate ion, H_2PO_4^- , fluoride ion, F^- , nitrite ion, NO_2^- , acetate ion, CH_3CO_2^- , hydrogen carbonate ion, HCO_3^- , hydrogen sulfide ion, HS^- , ammonia, NH_3 , cyanide ion, CN^- , carbonate ion, CO_3^{2-} , hydroxide ion (in blue), OH^- , sulfide ion, S^{2-} , ethoxide ion, $\text{C}_2\text{H}_5\text{O}^-$, amide ion NH_2^- , hydride ion, H^- , and methide ion CH_3^- . The bases at the top, from

perchlorate ion through nitrate ion are group with a bracket which is labeled “Do not undergo base ionization in water.” Similarly, the lower 5 in the listing, from sulfide ion through methide ion are grouped and labeled “Undergo complete base ionization in water.”

Figure 7.12.3 This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

If all these strong acids are completely ionized in water, why does the column indicate they vary in strength, with nitric acid being the weakest and perchloric acid the strongest? Notice that the sole acid species present in an aqueous solution of any strong acid is $\text{H}_3\text{O}^+(\text{aq})$, meaning that hydronium ion is the strongest acid that may exist in water; any stronger acid will react completely with water to generate hydronium ions. This limit on the acid strength of solutes in a solution is called a **leveling effect**. To measure the differences in acid strength for “strong” acids, the acids must be dissolved in a solvent that is *less basic* than water. In such solvents, the acids will be “weak,” and so any differences in the extent of their ionization can be determined. For example, the binary hydrogen halides HCl, HBr, and HI are strong acids in water but weak acids in ethanol (strength increasing $\text{HCl} < \text{HBr} < \text{HI}$).

The right column of Figure 7.12.3 lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don’t undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide). A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large K_a , and so its conjugate base will exhibit a K_b that is essentially zero:

- 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 7.12.2: Calculating Ionization Constants for Conjugate Acid-Base Pairs

Use the K_b for the nitrite ion, NO_2^- , to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11} .

The conjugate acid of NO_2^- 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.

? Exercise 7.12.2

Determine the relative acid strengths of NH_4^+ 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 NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3 , is listed as 1.8×10^{-5} .

Answer

NH_4^+ is the slightly stronger acid (K_a for NH_4^+ is 5.6×10^{-10}).

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.



This image shows two bottles containing clear colorless solutions. Each bottle contains a single pH indicator strip. The strip in the bottle on the left is red, and a similar red strip is placed on a filter paper circle in front of the bottle on surface on which the bottles are resting. Similarly, the second bottle on the right contains an orange strip and an orange strip is placed in front of it on a filter paper circle. Between the two bottles is a pack of pH Hydrion papers with a pH color scale on its cover.

This photo shows two glass containers filled with a transparent liquid. In between the containers is a pH strip indicator guide. There are pH strips placed in front of each glass container. The liquid in the container on the left appears to have a pH of 10 or 11. The liquid in the container on the right appears to have a pH of about 13 or 14.

Litmus paper in action

✓ Example 7.12.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (Figure 7.12.4) 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 7.12.4: Vinegar contains acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

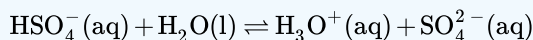
The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_a for acetic acid.

$$\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq})$$

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

? Exercise 7.12.3

The HSO_4^- 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:

$$[\text{H}_3\text{O}^+] = 0.027 \text{ M}; [\text{HSO}_4^-] = 0.29 \text{ M}; [\text{H}_2\text{SO}_4] = 0.29 \text{ M}; \text{ and } [\text{SO}_4^{2-}] = 0.13 \text{ M?}$$

Answer

$$K_a \text{ for } \text{HSO}_4^- = 1.2 \times 10^{-2}$$

✓ Example 7.12.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2] = 0.050 \text{ M}$, $[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+] = 5.0 \times 10^{-3} \text{ M}$, and $[\text{OH}^-] = 2.5 \times 10^{-3} \text{ M}$?

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.

$$\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$$

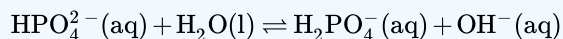
$$K_b = \frac{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+][\text{OH}^-]}{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2]}$$

$$= \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{(0.050)}$$

$$= 2.5 \times 10^{-4}$$

? Exercise 7.12.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base



if the composition of an equilibrium mixture is as follows: $[\text{OH}^-] =$

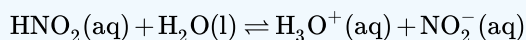
$$1.3 \times 10^{-6} \text{ M}; [\text{H}_2\text{PO}_4^-] = 0.042 \text{ M}; \text{ and } [\text{HPO}_4^{2-}] = 0.341 \text{ M?}$$

Answer

$$K_b \text{ for } \text{HPO}_4^{2-} \text{ is } 1.6 \times 10^{-7}$$

✓ Example 7.12.5: 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 ($1 \times 10^{-7} \text{ M}$) 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:

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

The ICE table for this system is then

	HNO_2	+	H_2O	\rightleftharpoons	H_3O^+	+	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

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following in the first column: Initial concentration (M), Change (M), Equilibrium concentration (M). The second column has the header of “H N O subscript 2 plus sign H subscript 2 O equilibrium sign H subscript 3 O superscript positive sign plus sign N O subscript 2 superscript negative sign.” Under the second column is a subgroup of four columns and three rows. The first column has the following: 0.0516, negative 0.0046, 0.0470. The second column is blank in all three rows. The third column has the following: approximately 0, positive 0.0046, 0.0046. The fourth column has the following: 0, positive 0.0046, 0.0046.

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

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

? Exercise 7.12.5

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

$$K_b = 1.8 \times 10^{-5}$$

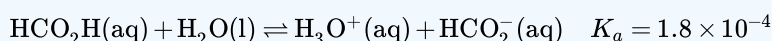
✓ Example 7.12.6: Calculating Equilibrium Concentrations in a Weak Acid Solution

Formic acid, HCO_2H , is one irritant that causes the body’s reaction to some ant bites and stings (Figure 7.12.5).



Figure 7.12.5 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

	$\text{HCO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_2^-$			
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:

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

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:

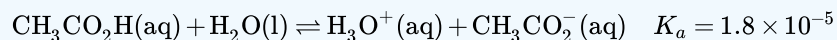
$$x = [\text{H}_3\text{O}^+] = 0.0098 \text{ M}$$

Finally, the pH is calculated to be

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

? Exercise 7.12.6

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 7.12.7: 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 (M)	0.25		0	~0
Change (M)	-x		x	x
Equilibrium concentration (M)	0.25 + (-x)		0 + x	~0 + x

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:

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

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:

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

permits the computation of pH:

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

? Exercise 7.12.7

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

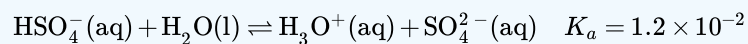
$$7.56 \times 10^{-4} \text{ M}, 2.33\%$$

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 7.12.8 below.

✓ Example 7.12.8: Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate, NaHSO_4 , is used in some household cleansers as a source of the HSO_4^- ion, a weak acid. What is the pH of a 0.50-M solution of HSO_4^- ?



Solution

The ICE table for this system is

	$\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$			
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

$$x = 0.077 \text{ M}$$

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:

$$\frac{x}{[\text{HSO}_4^-]_i} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15 (15\%)$$

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

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

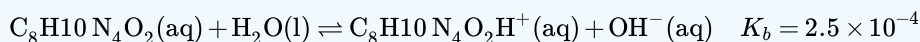
Solving for the two roots of this quadratic equation results in a negative value that may be discarded as physically irrelevant and a positive value equal to x . As defined in the ICE table, x is equal to the hydronium concentration.

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

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

? Exercise 7.12.8

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



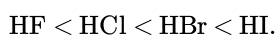
Answer

$$\text{pH} = 11.16$$

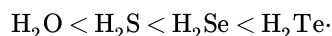
Effect of Molecular Structure on Acid-Base Strength

Binary Acids and Bases

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is



Likewise, for group 16, the order of increasing acid strength is



Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$; across the third row, it is $\text{SiH}_4 < \text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$ (see Figure 7.12.6).

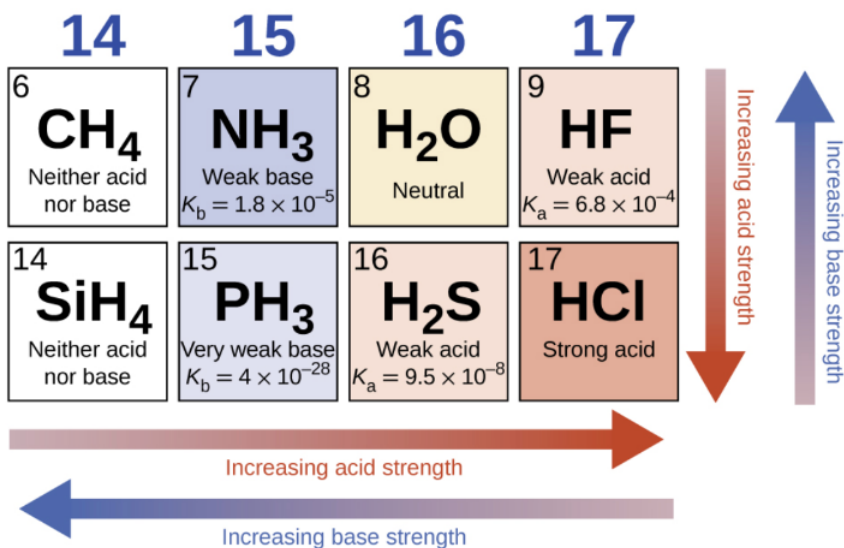
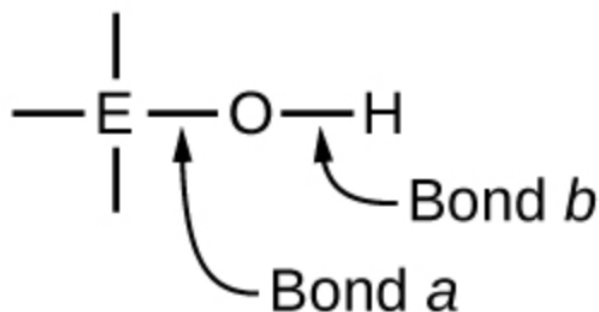


Figure 7.12.6 The figure shows trends in the strengths of binary acids and bases.

Ternary Acids and Bases

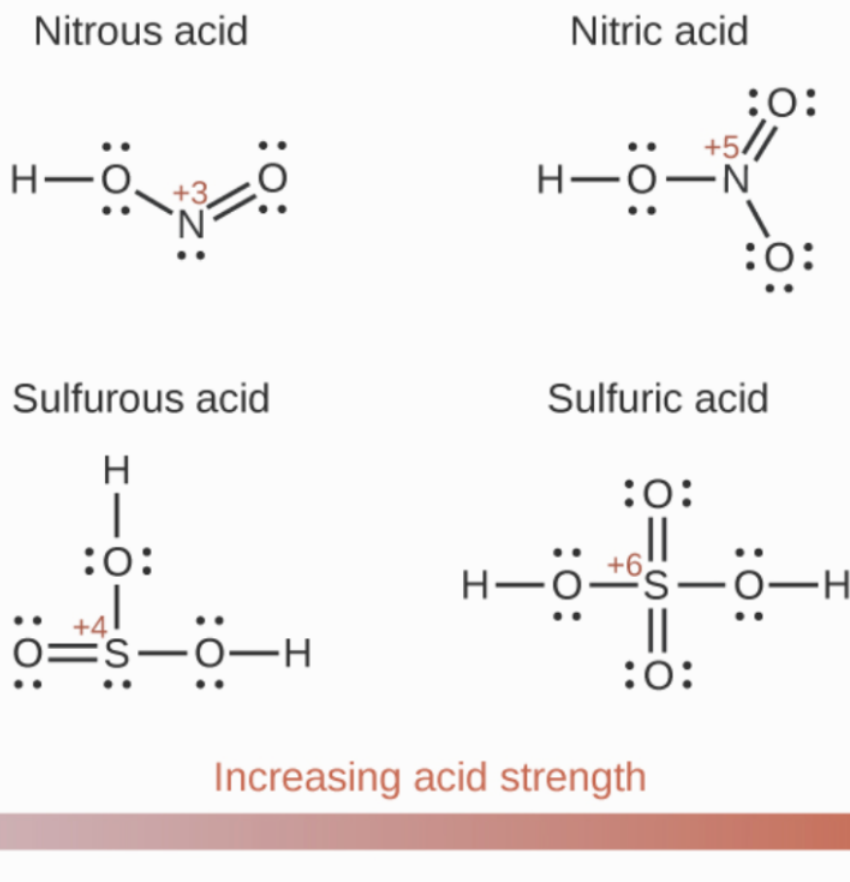
Ternary compounds composed of hydrogen, oxygen, and some third element ("E") may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, corresponding to the general molecular formula $\text{O}_m\text{E}(\text{OH})_n$. These compounds may be acidic, basic, or amphoteric depending on the properties of the central E atom. Examples of such compounds include sulfuric acid, $\text{O}_2\text{S}(\text{OH})_2$, sulfurous acid, $\text{OS}(\text{OH})_2$, nitric acid, O_2NOH , perchloric acid, O_3ClOH , aluminum hydroxide, $\text{Al}(\text{OH})_3$, calcium hydroxide, $\text{Ca}(\text{OH})_2$, and potassium hydroxide, KOH :



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $\text{Ca}(\text{OH})_2$ and KOH . Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic $-\text{OH}$ groups that are called oxyacids.

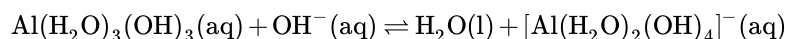
Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4 , or $\text{O}_2\text{S}(\text{OH})_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3 , or $\text{OS}(\text{OH})_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3 , or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2 , or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 7.12.7).



A diagram is shown that includes four structural formulas for acids. A red, right pointing arrow is placed beneath the structures which is labeled “Increasing acid strength.” At the top left, the structure of Nitrous acid is provided. It includes an H atom to which an O atom with two unshared electron pairs is connected with a single bond to the right. A single bond extends to the right and slightly below to a N atom with one unshared electron pair. A double bond extends up and to the right from this N atom to an O atom which has two unshared electron pairs. To the upper right is a structure for Nitric acid. This structure differs from the previous structure in that the N atom is directly to the right of the first O atom and a second O atom with three unshared electron pairs is connected with a single bond below and to the right of the N atom which has no unshared electron pairs. At the lower left, an O atom with two unshared electron pairs is double bonded to its right to an S atom with a single unshared electron pair. An O atom with two unshared electron pairs is bonded above and an H atom is single bonded to this O atom. To the right of the S atom is a single bond to another O atom with two unshared electron pairs to which an H atom is single bonded. This structure is labeled “Sulfurous acid.” A similar structure which is labeled “Sulfuric acid” is placed in the lower right region of the figure. This structure differs in that an H atom is single bonded to the left of the first O atom, leaving it with two unshared electron pairs and a fourth O atom with two unshared electron pairs is double bonded beneath the S atom, leaving it with no unshared electron pairs.

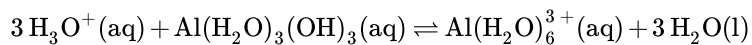
Figure 7.12.7: As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$, is converted into the soluble ion, $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$, by reaction with hydroxide ion:



In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is

converted to the soluble ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ by reaction with hydronium ion:



In this case, protons are transferred from hydronium ions in solution to $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$, and the compound functions as a base.

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