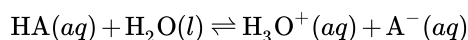


14.3: Relative Strengths of Acids and Bases

Learning Objectives

- 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

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

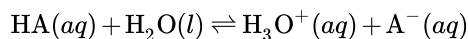


Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H_3O^+ and A^- when the acid ionizes in water; Figure 14.3.1 lists several strong acids. A weak acid gives small amounts of H_3O^+ and A^- .

Figure 14.3.1: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
HClO_4	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\text{Ca}(\text{OH})_2$	calcium hydroxide
HNO_3	nitric acid	$\text{Sr}(\text{OH})_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$\text{Ba}(\text{OH})_2$	barium hydroxide

The relative strengths of acids may be determined 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:



we write the equation for the ionization constant as:

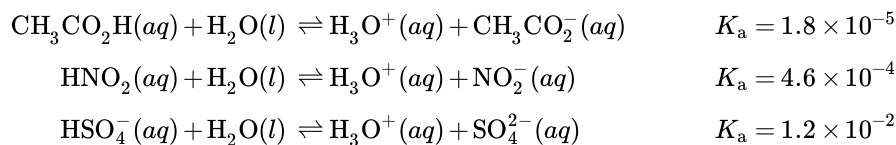
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

where the concentrations are those at equilibrium. As noted in the section on equilibrium constants, although water is a reactant in the reaction, it is the solvent as well, so its activity has a value of 1, which does not change the value of K_a .

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{\text{eq}}[\text{H}_2\text{O}]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{\text{eq}}(a_{\text{H}_2\text{O}})$. Because $a_{\text{H}_2\text{O}} = 1$ for a dilute solution, $K_a = K_{\text{eq}}(1)$, or $K_a = K_{\text{eq}}$.

The following data on acid-ionization constants indicate the order of acid strength: $\text{CH}_3\text{CO}_2\text{H} < \text{HNO}_2 < \text{HSO}_4^-$



Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100\% \quad (14.3.1)$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

✓ Example 14.3.1: Calculation of Percent Ionization from pH

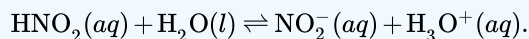
Calculate the percent ionization of a 0.125-M solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

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

The chemical equation for the dissociation of the nitrous acid is:



Since $10^{-\text{pH}} = [\text{H}_3\text{O}^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3} \text{ M}$, so that percent ionization (Equation 14.3.1) is:

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

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

? Exercise 14.3.1

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

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:



Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 14.3.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

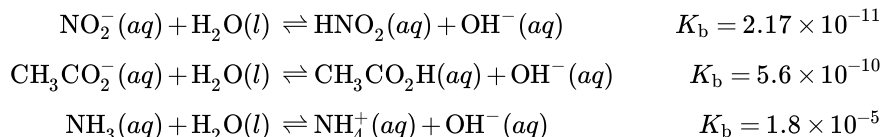
As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:



we write the equation for the ionization constant as:

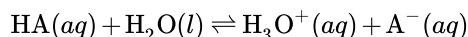
$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1. The chemical reactions and ionization constants of the three bases shown are:

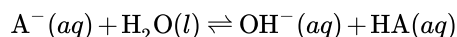


A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\text{HA} - \text{A}^-$:

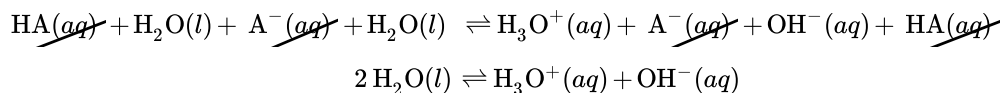


$$\text{with } K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$



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

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



As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

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

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5} , and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10} . The product of these two constants is indeed equal to K_w :

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

The extent to which an acid, HA , donates protons to water molecules depends on the strength of the conjugate base, A^- , of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^- . Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA , is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+ —the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 14.3.2).

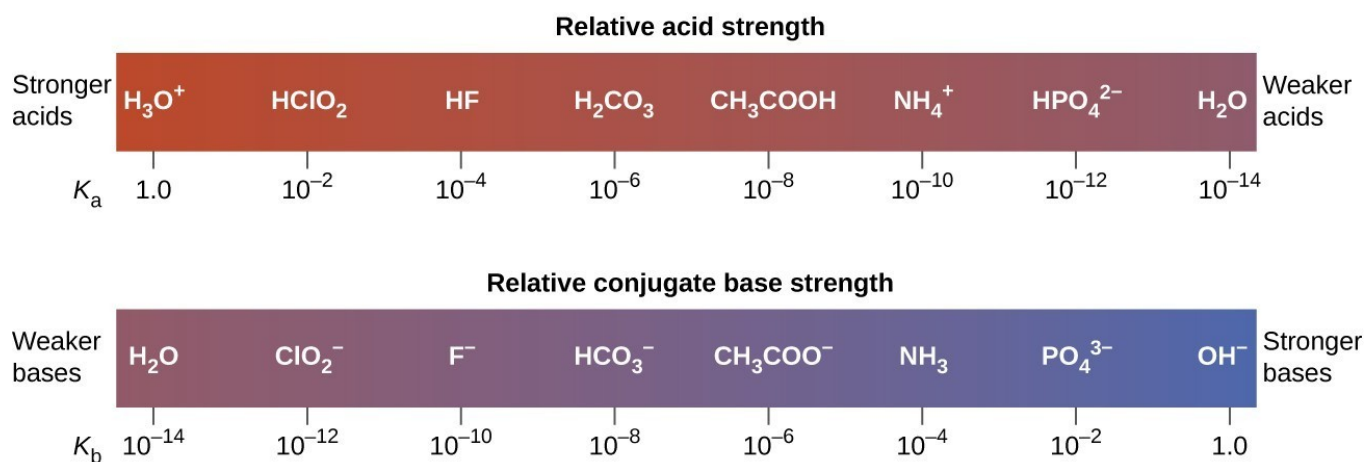


Figure 14.3.2: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 14.3.3 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure 14.3.3 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 14.3.3 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 14.3.3 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

Acid			Base		
Increasing acid strength ↑	perchloric acid	HClO ₄	Do not undergo base ionization in water	ClO ₄ ⁻	perchlorate ion
	sulfuric acid	H ₂ SO 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		NO ₃ ⁻	nitrate ion
	hydronium ion	H ₃ O ⁺		H ₂ O	water
	hydrogen sulfate ion	HSO ₄ ⁻		SO ₄ ²⁻	sulfate ion
	phosphoric acid	H ₃ PO ₄		H ₂ PO ₄ ⁻	dihydrogen phosphate ion
	hydrogen fluoride	HF		F ⁻	fluoride ion
	nitrous acid	HNO ₂		NO ₂ ⁻	nitrite ion
	acetic acid	CH ₃ CO ₂ H		CH ₃ CO ₂ ⁻	acetate ion
	carbonic acid	H ₂ CO ₃		HCO ₃ ⁻	hydrogen carbonate ion
	hydrogen sulfide	H ₂ S		HS ⁻	hydrogen sulfide ion
	ammonium ion	NH ₄ ⁺		HN ₃	ammonia
	hydrogen cyanide	HCN		CN ⁻	cyanide ion
	hydrogen carbonate ion	HCO ₃ ⁻		CO ₃ ²⁻	carbonate ion
	water	H ₂ O		OH ⁻	hydroxide ion
	hydrogen sulfide ion	HS ⁻	Undergo complete base ionization in water	S ²⁻	sulfide ion
	ethanol	C ₂ H ₅ OH		C ₂ H ₅ O ⁻	ethoxide ion
	ammonia	NH ₃		NH ₂ ⁻	amide ion
	hydrogen	H ₂		H ⁻	hydride ion
	methane	CH ₄		CH ₃ ⁻	methide ion

Figure 14.3.3: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 14.3.3. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

✓ Example 14.3.2: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO₂⁻, to calculate the K_a for its conjugate acid.

Solution

K_b for NO₂⁻ is given in this section as 2.17×10^{-11} . The conjugate acid of NO₂⁻ is HNO₂; K_a for HNO₂ can be calculated using the relationship:

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

Solving for K_a , we get:

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

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 14.3.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 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} . Determine the ionization constant of NH_4^+ , and decide which is the stronger acid, HCN or NH_4^+ .

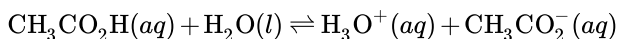
Answer

NH_4^+ is the slightly stronger acid (K_a for $\text{NH}_4^+ = 5.6 \times 10^{-10}$).

14.3.1: The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:



giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 14.3.4). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$



Figure 14.3.4: pH paper indicates that a 0.1-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[\text{H}_3\text{O}^+] = 0.1 \text{ M}$. A 0.1-M solution of $\text{CH}_3\text{CO}_2\text{H}$ (beaker on right) has a pH of 3 ($[\text{H}_3\text{O}^+] = 0.001 \text{ M}$) because the weak acid $\text{CH}_3\text{CO}_2\text{H}$ is only partially ionized. In this solution, $[\text{H}_3\text{O}^+] < [\text{CH}_3\text{CO}_2\text{H}]$. (credit: modification of work by Sahar Atwa)

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.

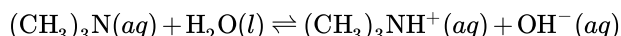
Table 14.3.1: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$	1.2×10^{-2}
$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$	3.5×10^{-4}
$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$	4.6×10^{-4}
$\text{HNC}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NCO}^-$	2×10^{-4}
$\text{HCO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_2^-$	1.8×10^{-4}
$\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^-$	1.8×10^{-5}
$\text{HClO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}^-$	2.9×10^{-8}
$\text{HBrO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{BrO}^-$	2.8×10^{-9}
$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$	4.9×10^{-10}

Table 14.3.1 gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(\text{CH}_3)_3\text{N}$, in water reacts according to the equation:



This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 14.4.5). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b , is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]}$$



Figure 14.3.5: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[\text{OH}^-] = 0.001 \text{ M}$) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table 14.3.2 and Table E2.

Table 14.3.2: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$	5.9×10^{-4}
$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$	4.4×10^{-4}
$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$	6.3×10^{-5}
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	4.3×10^{-10}

✓ Example 14.3.3: Determination of K_a from Equilibrium Concentrations

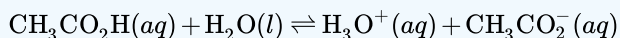
Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[\text{CH}_3\text{CO}_2\text{H}] = 0.0787 \text{ M}$ and $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CO}_2^-] = 0.00118 \text{ M}$. What is the value of K_a for acetic acid?



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

Solution

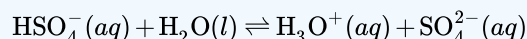
We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:



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

? Exercise 14.3.3

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:



In one mixture of NaHSO_4 and Na_2SO_4 at equilibrium, $[\text{H}_3\text{O}^+] = 0.027\text{ M}$; $[\text{HSO}_4^-] = 0.29\text{ M}$; and $[\text{SO}_4^{2-}] = 0.13\text{ M}$.

Answer

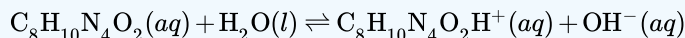
$$K_a \text{ for } \text{HSO}_4^- = 1.2 \times 10^{-2}$$

✓ Example 14.3.4: 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

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

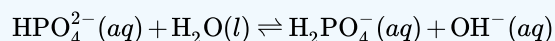


so

$$K_b = \frac{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+][\text{OH}^-]}{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

? Exercise 14.3.4

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



In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

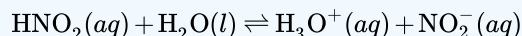
- $[\text{OH}^-] = 1.3 \times 10^{-6}\text{ M}$
- $[\text{H}_2\text{PO}_4^-] = 0.042\text{ M}$ and
- $[\text{HPO}_4^{2-}] = 0.341\text{ M}$.

Answer

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

✓ Example 14.3.5: Determination of K_a or K_b from pH

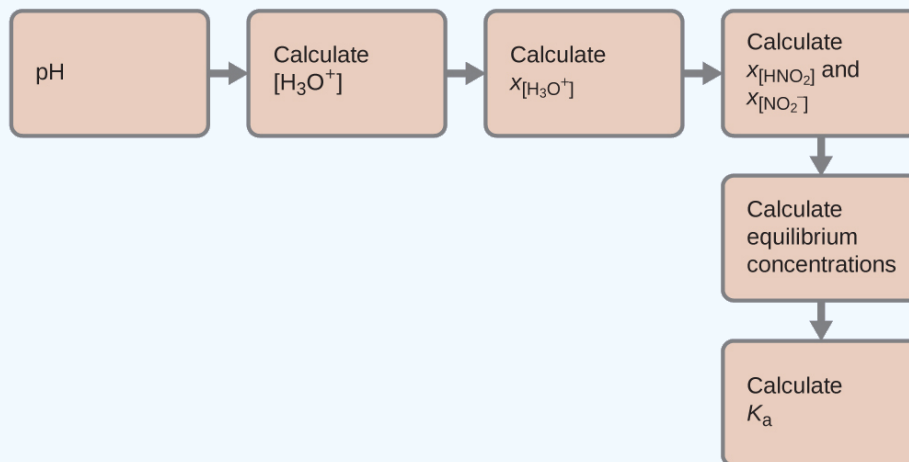
The pH of a 0.0516-M solution of nitrous acid, HNO_2 , is 2.34. What is its K_a ?



Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2 , H_3O^+ , and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which x is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here. Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction.

	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$			
Initial concentration (M)	0.0516		~ 0	0
Change (M)	$-x$	+	x	x
Equilibrium concentration (M)	$[\text{HNO}_2]_i + (-x) = 0.0516 + (-x)$		$[\text{H}_3\text{O}^+] + x[\text{NO}_2^-] + x \sim 0 + x$	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[\text{H}_3\text{O}^+]$, the equilibrium concentration of H_3O^+ , from the pH:

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

The change in concentration of H_3O^+ , $x_{[\text{H}_3\text{O}^+]}$, is the difference between the equilibrium concentration of H_3O^+ , which we determined from the pH, and the initial concentration, $[\text{H}_3\text{O}^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~ 0).

The change in concentration of NO_2^- is equal to the change in concentration of $[\text{H}_3\text{O}^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

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

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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

? Exercise 14.3.5

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

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

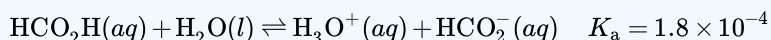
✓ Example 14.3.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H , is the irritant that causes the body's reaction to ant stings.



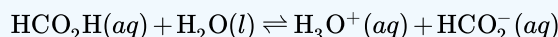
The pain of an ant's sting is caused by formic acid. (credit: John Tann)

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



Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:



Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

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

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$\begin{aligned}
 K_a &= 1.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} \\
 &= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}
 \end{aligned}$$

Now solve for x . Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x \ll 0.534$, which permits us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

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

Solve for x as follows:

$$\begin{aligned} x^2 &= 0.534 \times (1.8 \times 10^{-4}) \\ &= 9.6 \times 10^{-5} \\ x &= \sqrt{9.6 \times 10^{-5}} \\ &= 9.8 \times 10^{-3} \end{aligned}$$

To check the assumption that x is small compared to 0.534, we calculate:

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

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

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

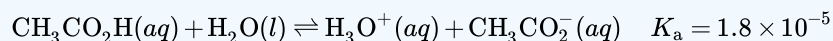
$$\begin{aligned} [\text{H}_3\text{O}^+] &= 0 + x = 0 + 9.8 \times 10^{-3} \text{ M} \\ &= 9.8 \times 10^{-3} \text{ M} \end{aligned}$$

The pH of the solution can be found by taking the negative log of the $[\text{H}_3\text{O}^+]$, so:

$$\text{pH} = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 14.3.6: acetic acid

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



Hint

Determine $[\text{CH}_3\text{CO}_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized $\times 100$, or $\frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]_{\text{initial}}} \times 100$.

Answer

percent ionization = 1.3%

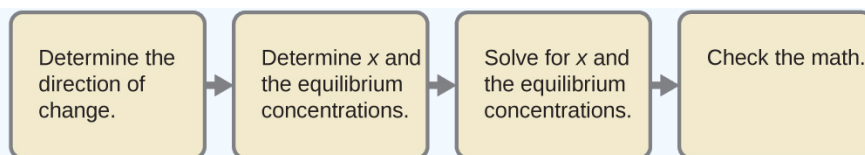
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 14.3.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-M solution of trimethylamine, a weak base:



Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 14.3.6. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

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

2. Solve for x and the equilibrium concentrations. At equilibrium:

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

If we assume that x is small relative to 0.25, then we can replace $(0.25 - x)$ in the preceding equation with 0.25. Solving the simplified equation gives:

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

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

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

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

Then calculate pOH as follows:

$$\text{pOH} = -\log(4.3 \times 10^{-3}) = 2.40$$

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:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

? Exercise 14.3.7

a. Show that the calculation in Step 2 of this example gives an x of 4.3×10^{-3} and the calculation in Step 3 shows $K_b = 6.3 \times 10^{-5}$.

b. Find the concentration of hydroxide ion in a 0.0325-M solution of ammonia, a weak base with a K_b of 1.76×10^{-5} .

Calculate the percent ionization of ammonia, the fraction ionized $\times 100$, or $\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \times 100\%$

Answer a

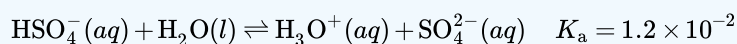
$$7.56 \times 10^{-4} \text{ M}, 2.33\%$$

Answer b

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

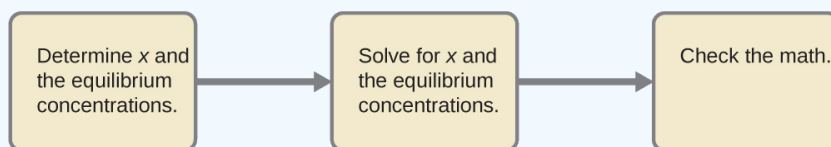
✓ Example 14.3.8: Equilibrium Concentrations in a Solution of a Weak Acid

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



Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[\text{H}_3\text{O}^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	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)	$0.50 + (-x) = 0.50 - x$				$0 + x = x$		$0 + x = x$

2. Solve for x and the concentrations.

As we begin solving for x , we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x .

At equilibrium:

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

If we assume that x is small and approximate $(0.50 - x)$ as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[\text{HSO}_4^-]_i} \stackrel{?}{\leq} 0.05$$

which for this system is

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

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x .

The equation:

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

gives

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

or

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

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

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

In this problem, $a = 1$, $b = 1.2 \times 10^{-2}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

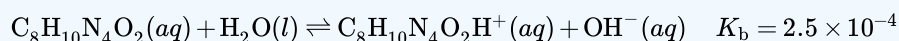
$$\begin{aligned} [\text{H}_3\text{O}^+] &= 0 + x = 0 + 7.2 \times 10^{-2} \text{ M} \\ &= 7.2 \times 10^{-2} \text{ M} \end{aligned}$$

The pH of this solution is:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 7.2 \times 10^{-2} = 1.14$$

? Exercise 14.3.8

- Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.
- Calculate the pH in a 0.010-M solution of caffeine, a weak base:



Hint

It will be necessary to convert $[\text{OH}^-]$ to $[\text{H}_3\text{O}^+]$ or pOH to pH toward the end of the calculation.

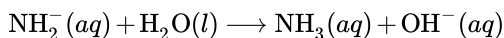
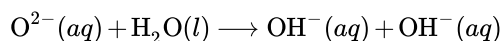
Answer

pH 11.16

14.3.2: The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^- , Br^- , and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order $\text{HCl} < \text{HBr} < \text{HI}$, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-} , and the amide ion, NH_2^- , are such strong bases that they react completely with water:



Thus, O^{2-} and NH_2^{-} appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

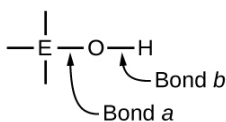
In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$. Likewise, for group 16, the order of increasing acid strength is $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$. 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 14.3.6).

14	15	16	17	
6 CH₄ Neither acid nor base	7 NH₃ Weak base $K_b = 1.8 \times 10^{-5}$	8 H₂O Neutral	9 HF Weak acid $K_a = 6.8 \times 10^{-4}$	<div style="display: flex; align-items: center;"> <div style="margin-right: 5px;">Increasing acid strength</div> <div style="flex-grow: 1; border-left: 2px solid red; position: relative;"> <div style="position: absolute; top: -10px; right: -10px;">↑</div> <div style="position: absolute; bottom: -10px; right: -10px;">↓</div> </div> </div>
14 SiH₄ Neither acid nor base	15 PH₃ Very weak base $K_b = 4 \times 10^{-28}$	16 H₂S Weak acid $K_a = 9.5 \times 10^{-8}$	17 HCl Strong acid	
<div style="display: flex; align-items: center; margin-top: 10px;"> <div style="margin-right: 5px;">Increasing acid strength</div> <div style="flex-grow: 1; border-top: 2px solid red; position: relative;"> <div style="position: absolute; left: -10px; bottom: -10px;">←</div> <div style="position: absolute; right: -10px; bottom: -10px;">→</div> </div> </div> <div style="display: flex; align-items: center; margin-top: 5px;"> <div style="margin-right: 5px;">Increasing base strength</div> <div style="flex-grow: 1; border-top: 2px solid blue; position: relative;"> <div style="position: absolute; left: -10px; bottom: -10px;">←</div> <div style="position: absolute; right: -10px; bottom: -10px;">→</div> </div> </div>				

Figure 14.3.6: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

This diagram has two rows and four columns. Red arrows point left across the bottom of the figure and down at the right side and are labeled “Increasing acid strength.” Blue arrows point left across the bottom and up at the right side of the figure and are labeled “Increasing base strength.” The first column is labeled 14 at the top and two white squares are beneath it. The first has the number 6 in the upper left corner and the formula C H subscript 4 in the center along with designation Neither acid nor base. The second square contains the number 14 in the upper left corner, the formula C H subscript 4 at the center and the designation Neither acid nor base. The second column is labeled 15 at the top and two blue squares are beneath it. The first has the number 7 in the upper left corner and the formula N H subscript 3 in the center along with the designation Weak base and K subscript b equals 1.8 times 10 superscript negative 5. The second square contains the number 15 in the upper left corner, the formula P H subscript 3 at the center and the designation Very weak base and K subscript b equals 4 times 10 superscript negative 28. The third column is labeled 16 at the top and two squares are beneath it. The first is shaded tan and has the number 8 in the upper left corner and the formula H subscript 2 O in the center along with the designation neutral. The second square is shaded pink, contains the number 16 in the upper left corner, the formula H subscript 2 S at the center and the designation Weak acid and K subscript a equals 9.5 times 10 superscript negative 8. The fourth column is labeled 17 at the top and two squares are beneath it. The first is shaded pink, has the number 9 in the upper left corner and the formula H F in the center along with the designation Weak acid and K subscript a equals 6.8 times 10 superscript negative 4. The second square is shaded a deeper pink, contains the number 17 in the upper left corner, the formula H C l at the center, and the designation Strong acid.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $\text{O}_n\text{E}(\text{OH})_m$, and 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:



A diagram is shown that includes a central atom designated with the letter E. Single bonds extend above, below, left, and right of the E. An O atom is bonded to the right of the E, and an arrow points to the bond labeling it, “Bond a.” An H atom is single bonded to the right of the O atom. An arrow pointing to this bond connects it to the label, “Bond b.”

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 14.3.7).

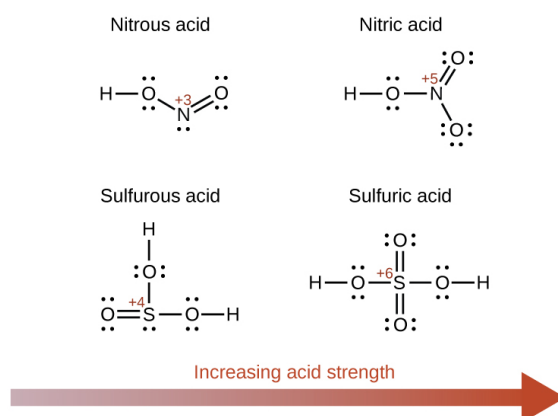
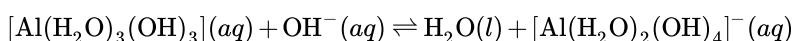


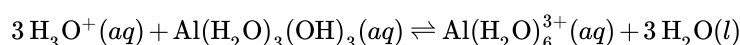
Figure 14.3.7: As the oxidation number of the central atom E increases, the acidity also increases.

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.

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.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$), and they increase down a group ($\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($\text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$\text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4$].

14.3.3: Key Equations

- $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
- $K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w$ (at room temperature)
- Percent ionization = $\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)

equilibrium constant for the ionization of a weak base

leveling effect of water

any acid stronger than H_3O^+ , or any base stronger than OH^- will react with water to form H_3O^+ , or OH^- , respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid

compound containing a nonmetal and one or more hydroxyl groups

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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