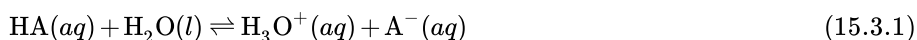


15.3: Acid and Base Strength

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:

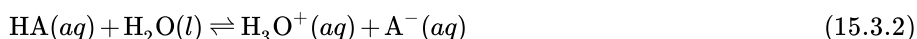


Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H_3O^+ and A^- when the acid ionizes in water; Figure 15.3.1 lists several strong acids. A weak acid gives small amounts of H_3O^+ and A^- .

Figure 15.3.1: 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:

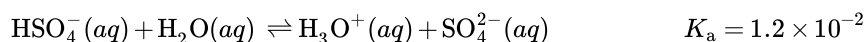
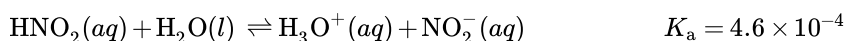
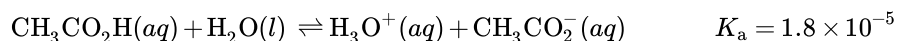


we write the equation for the ionization constant as:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad (15.3.3)$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is also the solvent. If the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. 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. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

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:

$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100\% \quad (15.3.4)$$

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 15.3.1: Calculation of Percent Ionization from pH

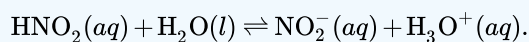
Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

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 15.3.4) 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.

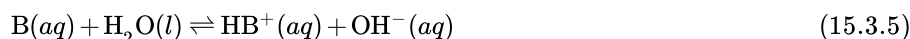
? Exercise 15.3.1

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

Answer

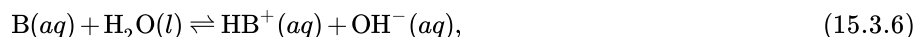
1.3% ionized

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 15.3.1 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.

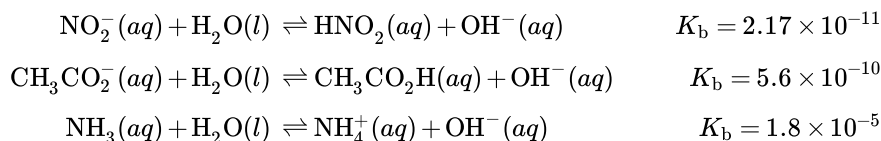
As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger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

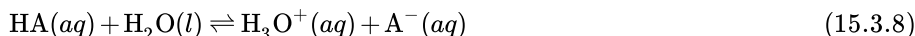
$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} \quad (15.3.7)$$

where the concentrations are those at equilibrium. Again, we do not include $[\text{H}_2\text{O}]$ in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

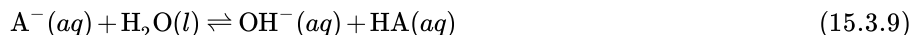


A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

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

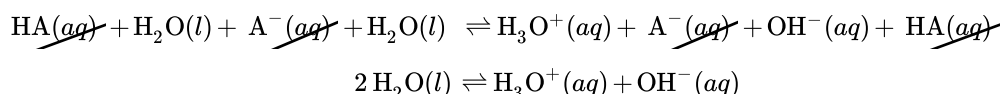


$$\text{with } K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$



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

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:

$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad (15.3.10)$$

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 :

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w \quad (15.3.11)$$

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 15.3.2).

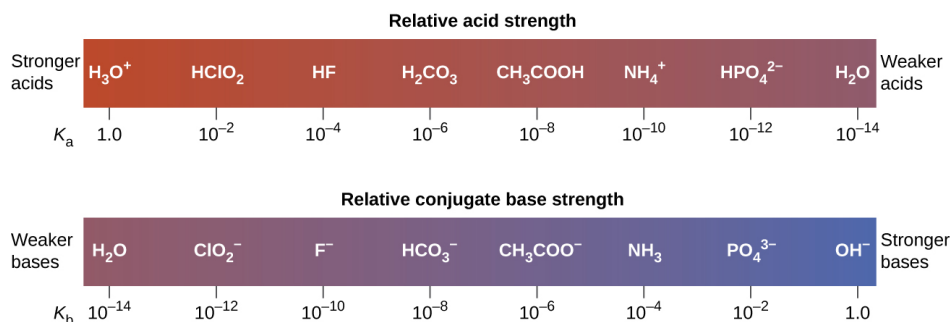


Figure 15.3.2: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 15.3.3 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 15.3.3 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 15.3.3 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 15.3.3 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 complete acid 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 ⁻	Undergo complete acid ionization in water	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 ⁺		NH 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 ⁻	Do not undergo complete acid 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 15.3.3: 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 15.3.3. 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 15.3.2: 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 15.3.2

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 $\text{NH}_4^+ = 5.6 \times 10^{-10}$).

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.

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)

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

percent ionization

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

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