5.3: Relative Strengths of Acids

Learning Objectives

- Distinguish between strong and weak acids
- Assess the relative strengths of acids according to their ionization constants

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:

$$\mathrm{HA}(aq)+\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)+\mathrm{A^-}(aq) \tag{5.3.1}$$

In these reactions, water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water.

5.3.1: Strong Acid Ionization

A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Table $5.3.1$ lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Table $5.3.1$: Some of the common strong acids and bases are listed here.

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

Because strong acids ionize completely in water, the pH of a strong acid solution can be found using the acid concentration.

$$[\mathrm{HA}]=[\mathrm{H_3O^+}] \tag{5.3.2}$$

Example $5.3.1$

What is the pH of concentrated hydrochloric acid, a 12.1 M solution?

Solution

Because hydrochloric acid is a strong acid, we know that $[\mathrm{HCl}]$ is equal to the hydronium concentration $[\mathrm{H_3O^+}]$.

$$[\mathrm{HCl}]=[\mathrm{H_3O^+}]=12.1\ M \tag{5.3.3}$$

$$pH=-log(12.1)=-1.083 \tag{5.3.4}$$

The pH of concentrated HCl is -1.083.

Exercise $5.3.1$

What is the pH of a 0.075 M solution of nitric acid?

Answer

pH = 1.12

5.3.2: The Ionization of Weak Acids

Many acids 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 non-ionized acid, hydronium ion, and the conjugate base of the acid, with the non-ionized acid present in the greatest concentration. 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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{5.3.5}$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \tag{5.3.6}$$

where the concentrations are those at equilibrium. 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.

Acetic acid ($\mathrm{CH_3CO_2H}$) is a familiar example of a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

giving an equilibrium mixture with most of the acid present in the non-ionized (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 $5.3.1$). The remaining weak acid is present in the non-ionized form.

For acetic acid, at equilibrium:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{CH_3CO_2^-}]}{[\mathrm{CH_3CO_2H}]} = 1.8 \times 10^{-5}$$

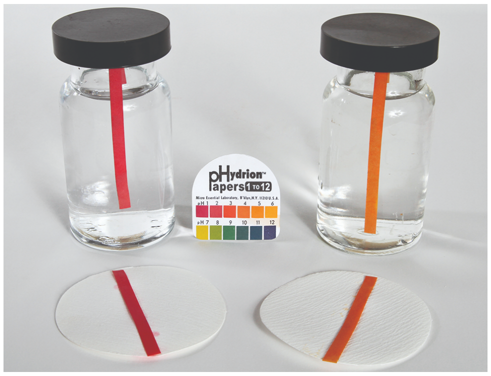


Figure $5.3.1$: pH paper indicates that a 0.l-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[\mathrm{H_3O^+}]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[\mathrm{H_3O^+}]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[\mathrm{H_3O^+}] < [\mathrm{CH_3CO_2H}]$. (credit: modification of work by Sahar Atwa)

Table $5.3.2$ gives the ionization constants for several weak acids; additional ionization constants can be found in the appendix of this text. Notice that all of the K_a values for weak acids are smaller than 1, indicating that the reactants side of the equilibrium reaction is favored. This is consistent with our definition of a weak acid: an acid that only partially ionizes in solution.

The strength of weak acids can be compared through their K_a values. The larger the K_a of an acid, the larger the concentration of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ relative to the concentration of the non-ionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid.

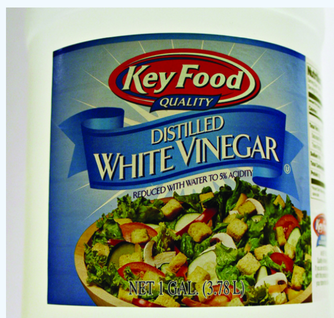
Table $5.3.2$: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$\mathrm{HSO_4^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{SO_4^{2-}}$	1.2×10^{-2}

Ionization Reaction	K_a at 25 °C
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5 × 10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6 × 10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2 × 10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8 × 10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8 × 10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9 × 10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8 × 10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9 × 10^{-10}

Example 5.3.2: 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 $[CH_3CO_2H]$ = 0.0787 M and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. 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:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$\begin{aligned} K_a &= \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} \\ &= \frac{(0.00118)(0.00118)}{0.0787} \\ &= 1.77 \times 10^{-5} \end{aligned}$$

Exercise 5.3.2

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

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 M; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$.

Answer

K_a for $HSO_4^- = 1.2 \times \times 10^{-2}$

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid ionization constants. 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. S

5.3.3: Key Equations

- $K_{\mathrm{a}} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid
