

Acid-Base Equilibria

The ionization of acids and dissociation of bases are reversible reactions. As such, they can be described by equilibrium expressions. The general reaction for an acid dissolved in water is as follows: $\text{HA}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$. $\text{HA}(aq)$ and $\text{A}^-(aq)$ are conjugate acid-base pairs, while $\text{H}_3\text{O}^+(aq)$ and $\text{H}_2\text{O}(\ell)$ are conjugate acid-base pairs. If $\text{A}^-(aq)$ is a much stronger base than $\text{H}_2\text{O}(\ell)$, then equilibrium lies to the left and most of the acid will be in the form $\text{HA}(aq)$, making $\text{HA}(aq)$ a weak acid. If $\text{H}_2\text{O}(\ell)$ is a much stronger base than $\text{A}^-(aq)$, then equilibrium lies to the right and the acid will be largely ionized, making $\text{HA}(aq)$ a strong acid. The acid ionization constant (K_a) comes from the equilibrium expression for the reaction. For acids, the higher the ionization constant is, the stronger the acid is. If the acid is ionized completely, $[\text{HA}] = 0$ and K_a is infinite. Ionization constants for very strong acids cannot be calculated.

Equilibrium Constants and Expressions

Acids

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

Bases

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

Water

$$K_w = [\text{H}^+][\text{OH}^-] = [\text{H}_3\text{O}^+][\text{OH}^-]$$

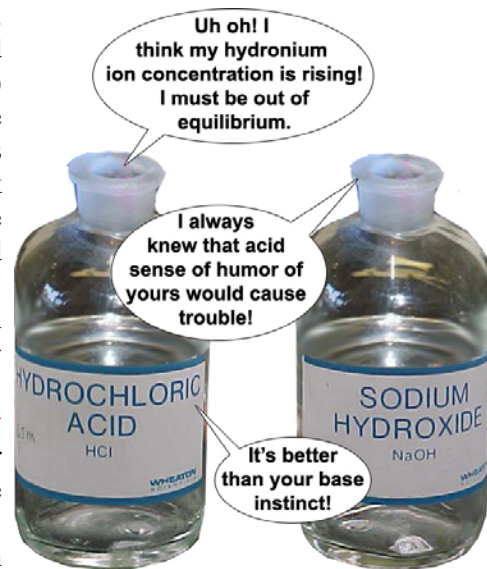
In that case, K_a is listed as “very large.” Ionization constants for acids that do NOT ionize completely can be calculated.

The general reaction between a base and water is $\text{B}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{BH}^+(aq) + \text{OH}^-(aq)$.

The equilibrium constant for the general reaction refers to the reaction of a base with water to form the conjugate acid and the hydroxide ion.

The ionization equation of water is the reversible reaction $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)$. At 25°C, $[\text{H}^+] = 1 \times 10^{-7} \text{ mol/L}$ and $[\text{H}^+] = [\text{OH}^-]$ in pure water. $K_w = [\text{H}^+][\text{OH}^-] = (1 \times 10^{-7} \text{ mol/L})(1 \times 10^{-7} \text{ mol/L}) = 1 \times 10^{-14} \text{ mol}^2/\text{L}^2$. The significance of this is, in any aqueous solution, no matter what else it contains, at 25°C, the product of $[\text{OH}^-]$ and $[\text{H}^+]$ is always 1.0×10^{-14} , resulting in three possible situations: [1] a neutral solution where $[\text{H}^+] = [\text{OH}^-]$; [2] an acidic solution where $[\text{H}^+] > [\text{OH}^-]$; and [3] a basic solution where $[\text{H}^+] < [\text{OH}^-]$. It is possible to calculate the concentration of hydronium or hydroxide when either one or the other ion's concentration is known.

$$[\text{H}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]} \text{ and } [\text{OH}^-] = \frac{1 \times 10^{-14}}{[\text{H}^+]}$$



Acid-Base banter

Answer the following questions based on your understanding of the equilibria involved.

- For the following strong acids and bases (100 percent ionized or dissociated), what are the hydronium and hydroxide ion concentrations?
 - $3.00 \times 10^{-4} \text{ M HNO}_3$ $[\text{H}_3\text{O}^+] =$ $[\text{OH}^-] =$
 - $2.50 \times 10^{-2} \text{ M Ca(OH)}_2$ $[\text{H}_3\text{O}^+] =$ $[\text{OH}^-] =$
 - $4.00 \times 10^{-3} \text{ M NaOH}$ $[\text{H}_3\text{O}^+] =$ $[\text{OH}^-] =$

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2. The equilibrium constant for nitrous acid (HNO_2), $K_a = 4.6 \times 10^{-4}$.
- Write the equation for the ionization of the acid in water. Identify the conjugate acid base pairs.
 - What is the hydronium ion concentration if $[\text{HNO}_2] = 3.00 \text{ M}$ and $[\text{NO}_2^-] = 0.037 \text{ M}$?
 - What is the hydroxide ion concentration based on the above concentrations?
3. The equilibrium constant for acetic acid (HCH_3COO), $K_a = 1.8 \times 10^{-5}$.
- Write the equation for the ionization of the acid in water. Identify the conjugate acid base pairs.
 - What is the hydronium ion concentration if $[\text{HCH}_3\text{COO}] = 2.50 \text{ M}$ and $[\text{CH}_3\text{COO}^-] = 0.027 \text{ M}$?
 - What is the hydroxide ion concentration based on the above concentrations?
4. The equilibrium constant for hydrofluoric acid (HF), $K_a = 3.5 \times 10^{-4}$.
- Write the equation for the ionization of the acid in water. Identify the conjugate acid base pairs.
 - What are the relative strengths of the conjugate acids and bases. Justify your response. _____

5. The equilibrium constants for hydrochloric acid and nitric acid are listed as “very large,” instead of having a numerical value. Why is this so? _____

