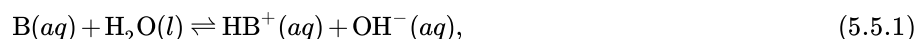


5.5: Relative Strengths of Bases

Learning Objectives

- Assess the relative strengths of bases according to their ionization constants
- Carry out equilibrium calculations for weak acid–base systems
- Calculate the K_b for the conjugate base of a weak acid

Bases act as proton acceptors. When in aqueous solutions, the water solvent can act as the acid that donates the proton to a base. 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:

$$K_b = \frac{[HB^+][OH^-]}{[B]} \quad (5.5.2)$$

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.

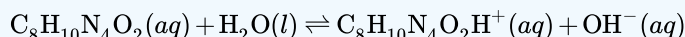
A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water, while a weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH and $Ca(OH)_2$ are considered strong bases because they dissociate completely when dissolved in water.

✓ Example 5.5.1: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050$ M, $[C_8H_{10}N_4O_2H^+] = 5.0 \times 10^{-3}$ M, and $[OH^-] = 2.5 \times 10^{-3}$ M?

Solution

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

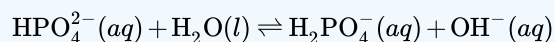


so

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4} \quad (5.5.3)$$

? Exercise 5.5.1

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:

- $[OH^-] = 1.3 \times 10^{-6}$ M
- $[H_2PO_4^-] = 0.042$ M and
- $[HPO_4^{2-}] = 0.341$ M.

Answer

$$K_b \text{ for } HPO_4^{2-} = 1.6 \times 10^{-7}$$

? Exercise 5.5.2

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

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

5.5.1: pH Calculations for Strong and Weak Bases

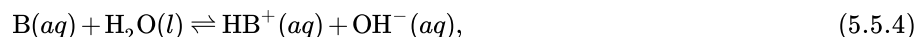
To determine the pH of a solution containing a strong base, the concentration of hydroxide ions, $[\text{OH}^-]$, is used to find the pOH.

$$\text{pOH} = -\log[\text{OH}^-]$$

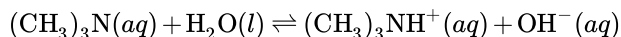
The pH and pOH are related through K_w , and so pH can be determined.

$$\text{pH} + \text{pOH} = 14$$

Weak bases cause only partial ionization. To determine the pH of a weak base solution we must utilize the base ionization constant. The reaction of a base, B, is:



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 5.5.1). 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 5.5.1: 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).

Table 5.5.1 contains ionization reactions and base ionization constants for select weak bases.

Table 5.5.1: 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}

Ionization Reaction	K_b at 25 °C
$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$	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}

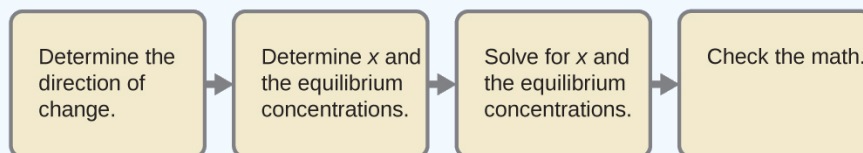
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 5.5.2: 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 5.5.6. 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:

$$\text{pOH} = -\log(4.0 \times 10^{-3}) = 2.40$$

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:

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

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

5.5.2: Percent Ionization for Bases

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.

$$\% \text{ ionization} = \frac{[\text{BH}^+]_{\text{eq}}}{[\text{B}]_0} \times 100\% \quad (5.5.5)$$

? Exercise 5.5.3

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 $\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \times 100\%$

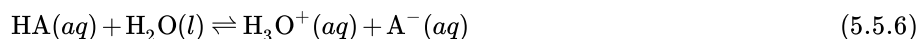
Answer

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

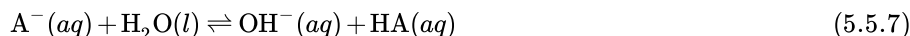
5.5.3: Ionization Constants for Conjugate Acid Base Pairs

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.

In an aqueous solution, the acid ionization constant for a particular acid (K_a) and the base ionization constant (K_b) for its conjugate base are related through K_w . Consider the ionization reactions for a conjugate acid-base pair, $\text{HA} - \text{A}^-$:

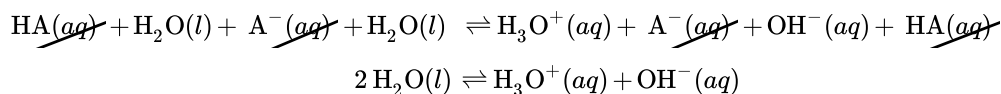


$$\text{with } K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$



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

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:

$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad (5.5.8)$$

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 :

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w \quad (5.5.9)$$

✓ Example 5.5.3: The Product $K_a \times K_b = K_w$

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 , 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 5.5.4

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

5.5.4: 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 [$\text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4$].

5.5.5: Key Equations

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

Glossary

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/base to the initial acid/base concentration, times 100

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