

Chapter 6 – Acids and Bases

Introduction

Brønsted acid-base reactions are proton transfer reactions. Acids donate protons to bases. In the process, the acid is converted into its conjugate base and the base into its conjugate acid. A conjugate acid-base pair differ by one and only one proton. The relative strength of an acid is given by its *acid dissociation constant*, K_a , which is the equilibrium constant for the reaction of the acid with the weak base water. In this chapter, we show how to use the K_a expression to determine equilibrium concentrations in solutions of acids and bases.

6.1 Autoionization of Water

Introduction

All of the acid-base reactions we will discuss occur in water, so it is important to understand the acid-base properties of water. Water is said to be *amphiprotic* because it can behave as either an acid or a base. In fact, the acidity of an aqueous solution is the extent to which water reacts with an acid to produce its conjugate acid H_3O^{1+} , the hydronium ion. Similarly, the basicity of a solution is the extent to which water reacts with a base to produce its conjugate base, OH^{1-} . In this section, we examine the relationship between the hydronium and hydroxide ion concentrations in aqueous solutions.

Objectives

- Convert between $[\text{H}_3\text{O}^{1+}]$ and $[\text{OH}^{1-}]$ in an aqueous solution.

6.1-1. Review of Acids and Bases

The following is a brief review of the more thorough treatment of acid-base chemistry which can be found in CAMS Chapter 12. You should refer to that chapter for a more in-depth discussion. The material in this and the following chapter assumes a knowledge of how to write chemical equations for acid-base reactions, so viewing the video in CAMS Section 12.8-1. would be especially helpful.

A Lewis base is a substance that contains a lone pair that can be used in a coordinate covalent bond, and a Lewis acid is a substance that has an empty orbital that can be used to share the lone pair in the bond. A Lewis acid-base reaction is the formation of the bond between the acid and the base. The Lewis acid-base reaction between ammonia and acetic acid is represented in Figure 6.1a. In it, the lone pair on ammonia is used to form a covalent bond to a hydrogen atom on the acetic acid. Ammonia contains the lone pair, so it is the base, and acetic acid accepts the lone pair, so it is the acid. In the reverse reaction a lone pair on the acetate ion attacks a proton of the ammonium ion in another Lewis acid-base reaction. This very broad classification allows us to treat many reactions as acid-base reactions. However, the reaction in the figure can also be viewed has a proton transfer from the acid to the base. Although proton transfer reactions can be viewed as Lewis acid-base reactions, a different acid-base theory was developed for this very important branch of chemistry.

In Brønsted-Lowery or simply Brønsted theory, an acid is a proton donor and a base is a proton acceptor. Acetic acid has a proton that it can transfer, so it is an acid, while ammonia can accept a proton, so it is a base. The loss of a proton converts the acid into its conjugate base, and the gain of the proton converts the base into its conjugate acid. An acid and a base differ by one proton only and are said to be a conjugate acid-base pair. The only reactants and products present in a Brønsted acid-base reaction are an acid, a base, and their conjugate base and acid. The brackets in Figure 6.1b identify the conjugate acid-base pairs in the reaction of acetic acid and ammonia.

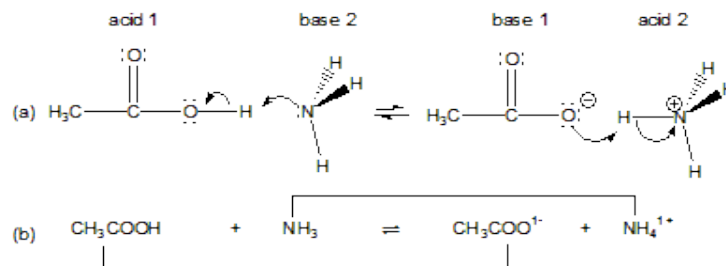
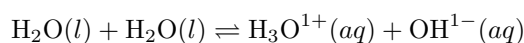


Figure 6.1: Acid-Base Reaction Between Acetic Acid and Ammonia (a) Lewis formalism (b) Brønsted formalism. The brackets connect conjugate acid-base pairs in the Brønsted formalism.

6.1-2. Ion Product Constant

K_w must be satisfied in all aqueous solutions.

Since water is both an acid and a base, it can react with itself in a process called *autoionization*.



The equilibrium constant expression for the autoionization, which is given in Equation 6.1, is called the *ion product constant of water* and given the symbol K_w . Water is the solvent, so it is treated as a pure liquid with an activity of unity, so it does not appear in the equilibrium constant expression.

$$K_w = \frac{[\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]}{1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}} \quad \text{Ion Product Constant for Water} \quad (6.1)$$

The subscript ‘w’ simply indicates ‘water’. It is called an ion product constant because it involves only the product of the concentrations of two ions. K_w must be satisfied in all aqueous solutions, regardless of what other substances may be dissolved. Thus, the hydronium and hydroxide ion concentrations in ALL aqueous solutions are related by Equation 6.1.

6.1-3. Acidity and Basicity

If water is the only source of H_3O^{1+} and OH^{1-} ions, then their concentrations must be equal because they are produced in a 1:1 ratio. However, addition of an acid to an aqueous solution increases $[\text{H}_3\text{O}^{1+}]$ and decreases $[\text{OH}^{1-}]$ so that the resulting concentrations obey Equation 6.1. Addition of a base has the opposite effect of increasing $[\text{OH}^{1-}]$ and decreasing $[\text{H}_3\text{O}^{1+}]$. Consequently, aqueous solutions can be classified as one of the following types.

- **Neutral Solution:** $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}]$
- **Acidic Solutions:** $[\text{H}_3\text{O}^{1+}] > [\text{OH}^{1-}]$
- **Basic Solutions:** $[\text{H}_3\text{O}^{1+}] < [\text{OH}^{1-}]$

However, Equation 6.1 is obeyed in all three types.

6.1-4. Exercise

EXERCISE: 6.1

What are the hydronium and hydroxide ion concentrations in pure water at 25 °C?

$$[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = \text{_____ } M$$

HCl is added to water until $[\text{H}_3\text{O}^{1+}] = 0.042 M$. What is the concentration of the hydroxide ion in the resulting solution at 25 °C?

$$[\text{OH}^{1-}] = \text{_____ } M$$

What is $[\text{H}_3\text{O}^{1+}]$ in a solution that is 0.50 M in hydroxide ion?

$$[\text{H}_3\text{O}^{1+}] = \text{_____ } M$$

6.2 The p-Scale

Introduction

Many of the numbers used in this chapter are very small, so they are often expressed on the p-scale to avoid the use of negative exponents or preceding zeroes.

Objective

- Determine $[\text{H}_3\text{O}^{1+}]$, $[\text{OH}^{1-}]$, pH, and pOH of a solution of a strong acid or strong base of known concentration.

6.2-1. Method for Converting to the p-Scale

The p-scale is defined in Equation 6.2. A 'p' placed before a concentration or a constant means that the number is the negative log of the concentration or constant.

$$\text{pX} = -\log(\text{X}) \quad \text{Converting a Number to the p-Scale} \quad (6.2)$$

For example, $\text{pH} = -\log [\text{H}_3\text{O}^{1+}]$ and $\text{p}K_{\text{a}} = -\log K_{\text{a}}$.

Taking the antilogarithm of both sides of Equation 6.2 gives the expression for converting the p-scale to the concentration or constant.

$$\text{X} = (10)^{-\text{pX}} \quad \text{Converting from the p-Scale Back to the Number} \quad (6.3)$$

The hydronium ion concentration in a solution with $\text{pH} = 3.20$ is $[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 10^{-3.20} = 6.3\text{e}-04$ and an acid with a $\text{p}K_{\text{a}} = 5.62$ has a $K_{\text{a}} = 10^{-5.62} = 2.4\text{e}-06$.

It might appear that the $[\text{H}_3\text{O}^{1+}]$ and K_{a} do not have the correct number of significant figures. After all, the pH has three, while the $[\text{H}_3\text{O}^{1+}]$ and K_{a} each have only two. The difference arises because the numbers to the left of the decimal in a logarithm indicate the exponent, not the significant figures. This is due to the way negative exponents are handled. An exponent of -3.20 is expressed as $0.80 - 4$, so $10^{-3.20} = (10^{0.80})(10^{-4}) = (6.3)(10^{-4})$. Thus, the significant figure, 6.3, is determined from 0.80, which comes from the 0.20 in the pH. The exponent, -4 , is dictated by the number to the left of the decimal.

We conclude that significant figures can be lost when converting from pX to X, while they can be gained in going from X to pX. This is the reason that $\text{p}K_{\text{a}}$ values are usually reported to three significant figures, while K_{a} values have only two.

The following are common uses of the p-scale.

$\text{pH} = -\log [\text{H}_3\text{O}^{1+}]$	$[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}}$
$\text{pOH} = -\log [\text{OH}^{1-}]$	$[\text{OH}^{1-}] = 10^{-\text{pOH}}$
$\text{p}K_w = -\log(K_w) = -\log(1.0 \times 10^{-14}) = 14.00$	$K_w = 10^{-\text{p}K_w} = 10^{-14}$
$\text{p}K_a = -\log(K_a)$	$K_a = 10^{-\text{p}K_a}$

Table 6.1

6.2-2. $\text{p}K_w$, pH, and pOH

We now express the ion product for water (Equation 6.1) in terms of pH and pOH.

$$K_w = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]$$

Taking the negative logarithm of both sides, we obtain the following.

$$-\log K_w = -\log [\text{H}_3\text{O}^{1+}] - \log [\text{OH}^{1-}]$$

Substitution of the p-scale definitions results in the relationship between pH, pOH, and $\text{p}K_w$.

$$\text{p}K_w = \text{pH} + \text{pOH} = 14.00 \text{ at } 25 \text{ }^\circ\text{C} \quad \text{p}K_w \quad (6.4)$$

Equation 6.4 is an important relationship that we will use to convert between the pH and pOH of aqueous solutions. It is important to realize that $\text{p}K_w = 14.00$ only at $25 \text{ }^\circ\text{C}$, but values at some selected temperatures are given in the following table.

T ($^\circ\text{C}$)	$\text{p}K_w$	K_w
0	14.94	1.15e-15
25	14.00	1.00e-14
50	13.28	5.25e-15
75	12.71	1.95e-13
100	12.26	5.50e-13

Table 6.2: $\text{p}K_w$ at Selected Temperatures

6.2-3. pH, Acidity, Basicity, and Neutrality

Acidic solutions: $[\text{H}_3\text{O}^{1+}] > 1.0 \times 10^{-7}$. Taking the negative logarithm of both sides of this inequality produces $\text{pH} < 7.00$ for acidic solutions. A solution in which $[\text{H}_3\text{O}^{1+}] = 1.0 \text{ M}$ ($\text{pH} = 0.0$) is fairly acidic solution, so most pH values for acidic solutions lie between 0 and 7. However, H_3O^{1+} concentrations greater than 1.0 M are possible. We conclude that **the pH of a solution decreases as the acidity increases, and the pH of most acidic solutions lies between 0 and 7, but negative values are possible.**

Basic Solutions: $[\text{OH}^{1-}] > 1.0 \times 10^{-7}$, so $[\text{H}_3\text{O}^{1+}] < 1.0 \times 10^{-7}$. Taking the negative logarithm of both sides yields $\text{pOH} < 7$ or $\text{pH} > 7$ for basic solutions. A solution in which $[\text{OH}^{1-}] = 1.0 \text{ M}$ has a $\text{pOH} = -\log(1.0) = 0.0$, which gives it a $\text{pH} = 14.0 - 0.0 = 14.0$, which is a very basic solution. However, solutions in which $[\text{OH}^{1-}] > 1 \text{ M}$ are not uncommon. We conclude that **the pH of a solution increases as the basicity increases, and the pH of most basic solutions lie between 7 and 14, but values higher than 14 are possible.**

Neutral Solutions: $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = 1.0 \times 10^{-7}$, so $\text{pH} = \text{pOH} = 7.00$ (at $25 \text{ }^\circ\text{C}$). Thus, **a neutral solution at $25 \text{ }^\circ\text{C}$ is one with $\text{pH} = 7.00$.**

These conclusions are summarized in the following figure.

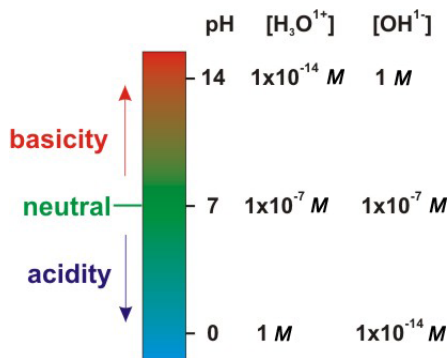


Figure 6.2: pH and Solution Type at 25 °C Pictured above is the relationship between pH, acidity, and basicity.

6.2-4. Converting to the p-Scale Exercises

EXERCISE 6.2:

Determine the pH and pOH of the following solutions.

Concentration	pH	pOH
[H ₃ O ¹⁺] = 1.0e-07 M	<input type="text"/>	<input type="text"/>
[H ₃ O ¹⁺] = 0.042 M	<input type="text"/>	<input type="text"/>
[OH ¹⁻] = 0.50 M	<input type="text"/>	<input type="text"/>

6.2-5. Exercise

EXERCISE 6.3:

What are [H₃O¹⁺] and [OH¹⁻] in a solution with a pH of 8.62?

[H₃O¹⁺] = _____ M [OH¹⁻] = _____ M
 pOH = _____

6.2-6. Exercise

EXERCISE 6.4:

The pH of a sample of lemon juice is found to be 2.32. What are the hydronium and hydroxide ion concentrations?

[H₃O¹⁺] = _____ M [OH¹⁻] = _____ M
 pOH = _____

6.2-7. Exercise

EXERCISE 6.5:

The hydroxide ion concentration in a bottle of household ammonia is 0.0083 M. Determine the pH, pOH, and the hydronium ion concentration of the solution.

$$\text{pOH} = \underline{\hspace{2cm}}$$

$$[\text{H}_3\text{O}^{1+}] = \underline{\hspace{2cm}} \text{ M}$$

$$\text{pH} = \underline{\hspace{2cm}}$$

6.3 Strong Acids

Introduction

The common strong acids are HClO_4 , HCl , HBr , HI , HNO_3 , and H_2SO_4 . In this section, we discuss how the pH of a strong acid solution is determined.

Objective

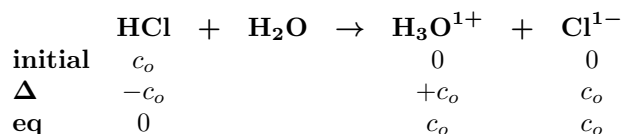
- Calculate the pH of the solutions of strong acids and of strong bases.

6.3-1. Strong Acid Video

A video or simulation is available online.

6.3-2. Strong Acid Solutions

Hydrochloric acid is a strong acid, so essentially all of the HCl reacts. The reaction is so extensive that it is usually represented with a single arrow.



In the reaction table above, c_o is the *makeup* concentration of the acid, which is the concentration given on the acid bottle. For strong, monoprotic acids, the hydronium ion concentration is given by the makeup concentration because all of the acid reacts. The case of H_2SO_4 is a little more complicated because only the first proton is strongly acidic. We will consider sulfuric acid in more detail in the section on polyprotic acids.

6.3-3. Exercises

EXERCISE 6.6:

What is the pH of a 0.16 M solution of hydrochloric acid?

$$\text{pH} = \underline{\hspace{2cm}}$$

6.4 Weak Acids

Introduction

Weak acids react only slightly with water, so the hydronium ion concentration in a solution of a weak acid does not equal the makeup concentration. In this section, we show how to determine the concentrations of all of the species in a solution of a weak acid.

Objectives

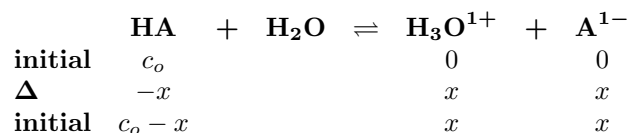
- Write the K_a expression for a weak acid.
- Determine the equilibrium concentrations of all species present in and the pH of solutions of weak acids.
- Determine the pH, K_a , or initial concentration of a weak acid solution given the other two.
- Calculate the percent ionization of a weak acid.
- Convert between pK_a and K_a .

6.4-1. Weak Acid Video

A video or simulation is available online.

6.4-2. Weak Acid-Water Reaction Table

The equilibrium constant for the reaction of an acid and water is called the acid dissociation constant, K_a . K_a is so large for strong acids that all of the acid reacts to produce hydronium ion and the conjugate base of the acid. K_a is small for weak acids, so only a portion of a weak acid reacts with water. Thus, the Δ line entries of the reaction table are unknown. Consider the reaction of a generic weak acid HA with water.



Water is the solvent, so it is treated as a pure liquid (activity = 1), so the K_a expression is the following.

$$K_a = \frac{[\text{H}_3\text{O}^{1+}][\text{A}^{1-}]}{[\text{HA}]} = \frac{(x)(x)}{c_o - x} = \frac{x^2}{c_o - x} \quad \text{Acid Dissociation Expression} \quad (6.5)$$

The values of K_a and pK_a for several acids are given in the Acid-Base Table with pK_a .

6.4-3. Solving the K_a Expression

We must solve Equation 6.5 for x to obtain the equilibrium concentrations in an aqueous solution of the weak acid HA.

$$K_a = \frac{x^2}{c_o - x}$$

where $x = [\text{H}_3\text{O}^{1+}] = [\text{A}^{1-}]$ and $c_o - x = [\text{HA}]$. The equation is a quadratic that could be solved by gathering terms and using the quadratic formula. However, it can be solved more simply if x is negligible compared to c_o , i.e., if $c_o - x \sim c_o$. In other words, if so little of the acid reacts that the acid concentration is essentially unchanged. Making this substitution, we obtain the following expression for a weak acid

$$K_a = \frac{x^2}{c_o}$$

which can be solved for x , the concentration of the hydronium ion or the conjugate base (A^{1-}), with Equation 6.6.

$$[\text{H}_3\text{O}^{1+}] = [\text{A}^{1-}] = \sqrt{K_a c_o} \quad \text{Concentrations in an Aqueous Solution of HA} \quad (6.6)$$

Although neglecting x in the $c_o - x$ term is acceptable most of the time, there are times (K_a is large or c_o is small) when x is not negligible. Consequently, you should use the above expression only when solving for the squared term, and you should always check your result to see if it is indeed negligible. An easy way to determine whether the approximation is valid is given next.

6.4-4. Five Percent Rule

Equation 6.6 is an easy way to determine the concentrations in a solution of a weak acid, but the approximation used to derive it is not always valid, so the answer should always be checked. There are two ways to check whether x is negligible:

- **Inspection:** The value of x calculated with Equation 6.6 is often so small that it is obviously negligible compared to c_o . For example, if $c_o = 0.100\text{ M}$ and $x = 0.0000001\text{ M}$ then $c_o - x = 0.100\text{ M}$ and the assumption is good.
- **5% Rule:** If x is less than 5% of c_o , then approximating c_o for $c_o - x$ will produce the same answer as the quadratic formula. For example, substitution of $c_o = 0.100$ and $K_a = 1.6\text{e-}04$ into Equation 6.6 gives $x = 0.004\text{ M}$. In this case, $c_o - x = 0.100 - 0.004 = 0.096$, which is not equal to c_o . However, $(x/c_o) = 0.04$, which is 4%. Thus, x is less than 5%, so using the quadratic formula would result in the same answer for x .

6.4-5. Solving Without Approximation

If the answer produced by Equation 6.6 is greater than 5% of c_o , the terms in Equation 6.5 must be gathered in the form of a quadratic equation ($ax^2 + bx + c = 0$) and solved with the quadratic formula given below.

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

However, Equation 6.6 is so easy to use, that it is usually simpler to use it and check to be certain that x is within the 5% limit. This is especially true since most of the acids and concentrations we deal with in this course are so weak that the 5% rule is usually obeyed. However, for the stronger of the weak acids or for very dilute solutions, more than 5% of the acid may react, so always check.

6.4-6. Method for Weak Acid Problems

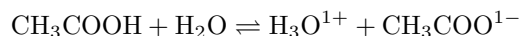
Equations 6.5 and 6.6 indicate that three terms (c_o , x , and K_a) are required to establish a weak acid equilibrium. Consequently, there are three different types of problems that are solved using these equations. The three differ in the identity of the unknown.

- x : What is the pH, $[\text{H}_3\text{O}^{1+}]$, or $[\text{A}^{1-}]$? Given: K_a (or the identity of the acid so you can look it up) and the makeup concentration. Method: Use Equation 6.6 to solve for the unknown then check that x is indeed small enough to neglect. If x is not small enough, rearrange the expression so that it is in the form of a quadratic equation and use the quadratic formula to solve for the unknown concentration.
- K_a : What is the value of K_a ? Given: x as the pH, $[\text{H}_3\text{O}^{1+}]$, or $[\text{A}^{1-}]$ and the makeup concentration. Method: Substitute the known values into Equation 6.5. Since x and c_o are known, there is no reason to make the neglect- x approximation, so make the subtraction.
- c_o : How much acid must be used to make a solution? Given: x as pH, $[\text{H}_3\text{O}^{1+}]$, or $[\text{A}^{1-}]$, and K_a (or the identity of the acid so you can look it up). Method: Solve Equation 6.5 for the equilibrium concentration of the weak acid ($c_o - x$), then solve for c_o using the given value of x .

6.4-7. Determining the pH Exercise

EXERCISE 6.7:

What is the pH of a 0.10-*M* solution of acetic acid?



First, look up the K_a of acetic acid in the resource titled Acid-Base Table with pK_a .

$$K_a = \underline{\hspace{2cm}}$$

Then use Equation 6.6 with the K_a and the given initial concentration to determine $x = [\text{H}_3\text{O}^{1+}]$.

$$[\text{H}_3\text{O}^{1+}] = \underline{\hspace{2cm}} \text{ M}$$

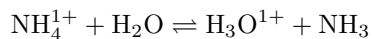
Finally, convert $[\text{H}_3\text{O}^{1+}]$ into pH.

$$\text{pH} = \underline{\hspace{2cm}}$$

6.4-8. Determining the pH Exercise

EXERCISE 6.8:

What is the pH of a 0.080-*M* solution of ammonium nitrate? Ammonium ion is a weak acid.



(The relevant pK_a can be found in the Acid-Base Table with pK_a .)

$$K_a = \underline{\hspace{2cm}}$$

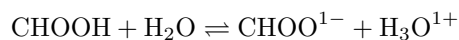
$$\text{pH} = \underline{\hspace{2cm}}$$

$$[\text{H}_3\text{O}^{1+}] = \underline{\hspace{2cm}} \text{ M}$$

6.4-9. Determining K_a Exercise

EXERCISE 6.9:

If a 0.0750-*M* solution of formic acid has a pH of 2.447, what is the K_a of formic acid?



The equilibrium concentrations are as follows.

$$[\text{H}_3\text{O}^{1+}] = \underline{\hspace{2cm}} \text{ M}$$

$$[\text{CHOOH}] = \underline{\hspace{2cm}} \text{ M}$$

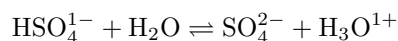
$$[\text{CHOO}^{1-}] = \underline{\hspace{2cm}} \text{ M}$$

$$K_a = \underline{\hspace{2cm}}$$

6.4-10. Determining the Makeup Concentration Exercise

EXERCISE 6.10:

What initial concentration of a KHSO_4 solution would be required to make a $\text{pH} = 2.00$ solution?



(The relevant $\text{p}K_a$ can be found in the Acid-Base Table with $\text{p}K_a$.)

$$K_a = \underline{\hspace{2cm}}$$

The equilibrium concentrations are as follows.

$$[\text{H}_3\text{O}^{1+}] = \underline{\hspace{2cm}} M$$

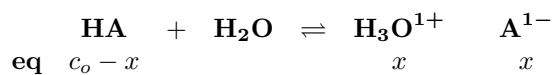
$$[\text{HSO}_4^{1-}] = \underline{\hspace{2cm}} M$$

$$[\text{SO}_4^{2-}] = \underline{\hspace{2cm}} M$$

$$c_o = \underline{\hspace{2cm}}$$

6.4-11. Percent Ionization

We now show that the fraction of an acid that reacts depends upon both its concentration and its acid dissociation constant. We start by reproducing the equilibrium line in the reaction table for a weak acid reacting with water.



Of the initial concentration c_o , x mol/L react, so the fraction that reacts is x/c_o . If we assume that the amount that reacts is negligible ($c_o - x = c_o$), we can use Equation 6.6 to determine x as $(c_o K_a)^{1/2}$. Substitution of this value of x into the expression for the fraction that reacts produces the following.

$$\text{fraction dissociating} = \frac{x}{c_o} = \frac{\sqrt{K_a c_o}}{c_o} = \sqrt{\frac{K_a}{c_o}}$$

Multiplication of the above by 100% gives us the percent ionization (reaction) of a weak acid.

$$\text{percent ionization} = \sqrt{\frac{K_a}{c_o}} \times 100\% \quad \text{Percent Ionization of a Weak Acid} \quad (6.7)$$

Note that the percent that reacts depends upon both K_a and c_o . Thus, the 5% rule is obeyed by acids with low K_a values and relatively high concentrations. Consider the following table that compares the percent ionization of nitrous ($K_a = 4.0\text{e-}4$), acetic ($K_a = 1.8\text{e-}5$), and hypochlorous ($K_a = 3.5\text{e-}8$) acids as a function of their concentrations.

Molarity	HNO_2	CH_3COOH	HOCl
1.0	2.0%	0.42%	0.019%
0.10	6.1%*	1.3%	0.059%
0.010	18%*	4.2%	0.19%
0.00010	83%*	34%*	1.9%

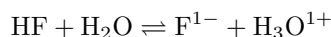
Table 6.3: Percent Ionization of Selected Acids

*The percent ionization exceeds 5% in these cases, so the quadratic formula was used to determine x .

6.4-12. Percent Ionization Exercise

EXERCISE 6.11:

What is the percent ionization and pH of 0.026 M HF? (The relevant pK_a can be found in the Acid-Base Table with pK_a .)



$$K_a = \underline{\hspace{2cm}}$$

$$\% \text{ dissociation using Equation 6.7} = \underline{\hspace{2cm}} \%$$

Is Equation 6.7 valid for this solution?

Yes

No

$$[\text{H}_3\text{O}^{1+}] \text{ using the quadratic formula} = \underline{\hspace{2cm}} M$$

$$\% \text{ dissociation} = \underline{\hspace{2cm}} \%$$

$$\text{pH} = \underline{\hspace{2cm}}$$

6.5 Polyprotic Acids

Introduction

Polyprotic acids contain two or more protons. For example, H_2S is diprotic and H_3PO_4 is triprotic. There are some polyprotic acids that contain more than three protons, but we will not consider any of these acids. The conjugate base of a polyprotic acid is also an acid, and the solution of a polyprotic acid is really a solution of more than one acid. Although it might seem that this would make the treatment of these acids very difficult, determining the concentrations of the species present in a polyprotic acid is not much different than determining the concentrations in a solution of a monoprotic acid.

Objective

- Determine the concentrations of all species in a solution of a polyprotic acid of known concentration.

6.5-1. Phosphoric Acid Overview

We examine a 0.10-M solution of phosphoric acid as an example because it contains three protons and is the most complicated. The three deprotonation steps are the following.

$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^{1-} + \text{H}_3\text{O}^{1+}$	$K_1 = 7.5 \times 10^{-5}$
$\text{H}_2\text{PO}_4^{1-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^{1+}$	$K_2 = 6.2 \times 10^{-8}$
$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{PO}_4^{3-} + \text{H}_3\text{O}^{1+}$	$K_3 = 4.8 \times 10^{-13}$

Note that each K value is over 1,000 times smaller than the preceding value. This is the case for most polyprotic acids, and it is why polyprotic acids can be treated in a relatively simple manner. The large decrease in K means that a negligible amount of each acid reacts in each step, so the concentration of any species is the concentration determined in the first step in which it is produced. The method we will use to find the concentrations of all species is the following:

- 1 Determine $[\text{H}_3\text{O}^{1+}]$, $[\text{H}_2\text{PO}_4^{1-}]$, and $[\text{H}_3\text{PO}_4]$ from the first acid dissociation. These concentrations are not affected by subsequent steps because the subsequent equilibrium constants are so small.
- 2 Set up the reaction table for the second reaction using the $[\text{H}_3\text{O}^{1+}]$ and $[\text{H}_2\text{PO}_4^{1-}]$ determined in step 1 as the initial conditions. Solve the equilibrium problem for $[\text{HPO}_4^{2-}]$, which will be shown to equal K_2 .

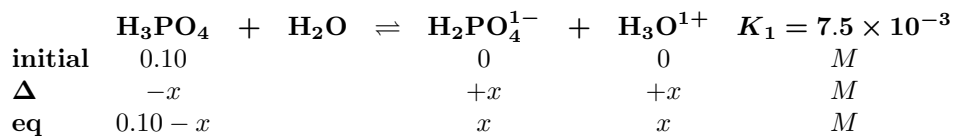
- 3 Set up the reaction table for the third reaction using $[\text{H}_3\text{O}^{1+}]$ and $[\text{HPO}_4^{2-}]$ determined in steps 1 and 2 as initial concentrations. Solve the equilibrium problem for $[\text{PO}_4^{3-}]$.

We next examine each of these steps more closely.

6.5-2. Phosphoric Acid Step 1

Essentially all of the hydronium ion in a solution of a polyprotic acid is produced in the first deprotonation step.

The reaction table for the first step in the deprotonation of 0.10 M H_3PO_4 is as follows.



H_3PO_4 is about five hundred times stronger than acetic acid so x is probably not negligible in a 0.10 M solution, but we try the approximation to be sure.

$$x = (c_o K_a)^{1/2} = (0.10)(7.5e-3)^{1/2} = 0.027 M$$

The result represents a 27% dissociation, which is well above the 5% limit. The approximation cannot be used, so we must solve for x with the quadratic formula as follows:

- 1 Set up the K_a expression.

$$7.5e-3 = \frac{x^2}{0.10 - x}$$

- 2 Multiply both sides by $(0.10 - x)$ to get x out of the denominator.

$$(7.5e-3)(0.10 - x) = x^2$$

- 3 Carry out the multiplication on the left side.

$$7.5e-4 - 7.5e-3x = x^2$$

- 4 Gather terms in the form of a quadratic equation.

$$x^2 + 7.5e-3x - 7.5e-4 = 0$$

- 5 Compare the above to the quadratic equation to obtain the following.

$$a = 1, b = 7.5e-3, \text{ and } c = -7.5e-4$$

- 6 Use these values in quadratic formula to obtain the following.

$$x = [\text{H}_3\text{O}^{1+}] = [\text{H}_2\text{PO}_4^{1-}] = 0.024 M$$

- 7 Use $[\text{H}_3\text{PO}_4] = c_o - x$ to obtain the following.

$$[\text{H}_3\text{PO}_4] = 0.10 - 0.02 = 0.08 M$$

Next we use these concentrations in the second deprotonation.

6.5-3. Phosphoric Acid Step 2

The reaction table for the second deprotonation step is the same as that for the dissociation of $0.024\text{ M H}_2\text{PO}_4^{1-}$ except that the initial concentration of $[\text{H}_3\text{O}^{1+}]$ is also 0.024 M as a result of the dissociation of H_3PO_4 .

	$\text{H}_2\text{PO}_4^{1-}$	+	H_2O	\rightleftharpoons	HPO_4^{2-}	+	$[\text{H}_3\text{O}^{1+}]$	$K_2 = 6.2 \times 10^{-8}$
initial	0.024				0		0.024	M
Δ	$-x$				0		$+x$	M
eq	$0.024 - x$				x		$0.024 + x$	M

Set up the equilibrium constant expression.

$$K_a = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_2\text{PO}_4^{1-}]}$$

Substitute the given K_a and the entries in the equilibrium line.

$$6.2\text{e-}8 = \frac{x(0.024 + x)}{0.024 - x}$$

If x is negligible then $0.024 + x = 0.024 - x$ and the two terms cancel in the K_2 expression to yield $[\text{HPO}_4^{2-}] = K_2 = 6.2\text{e-}8$, which is certainly negligible compared to 0.024 .

We conclude the following.

The concentration of the ion produced in the second deprotonation of a polyprotic acid equals K_2 , the equilibrium constant for the deprotonation.

6.5-4. Phosphoric Acid Step 3

The reaction table for the third deprotonation step is the same as dissociation of HPO_4^{2-} except that the initial concentration of $[\text{H}_3\text{O}^{1+}]$ is 0.024 M from the first step and that of $\text{H}_2\text{PO}_4^{1-}$ is $6.2\text{e-}8\text{ M}$ as a result of the second step.

	HPO_4^{2-}	+	H_2O	\rightleftharpoons	PO_4^{3-}	+	$[\text{H}_3\text{O}^{1+}]$	$K_3 = 4.8 \times 10^{-13}$
initial	$6.2\text{e-}8$				0		0.024	M
Δ	$-x$				$+x$		$+x$	M
eq	$6.2\text{e-}8$				x		0.024	M

x has been assumed to be negligible compared to the initial concentrations. Set up the equilibrium constant expression.

$$K_3 = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^{1+}]}{[\text{HPO}_4^{2-}]}$$

Substitute the given K_a and the entries in the equilibrium line.

$$4.8\text{e-}13 = \frac{x(0.024)}{(6.2\text{e-}8)}$$

Solve for $x = [\text{PO}_4^{3-}]$ to obtain

$$[\text{PO}_4^{3-}] = \frac{(4.8\text{e-}13)(6.2\text{e-}8)}{(0.024)} = 1.2\text{e-}18\text{ M}$$

which is negligible. Indeed, there is hardly any phosphate ion present in 0.1 M phosphoric acid. In summary, the concentrations of the phosphorus containing species are as follows.

- $[\text{H}_3\text{PO}_4] = 0.08\text{ M}$

- $[\text{H}_2\text{PO}_4^{1-}] = 0.024 \text{ M}$
- $[\text{HPO}_4^{2-}] = 6.2\text{e-}8 \text{ M}$
- $[\text{PO}_4^{3-}] = 1.2\text{e-}18 \text{ M}$

Note that the sum of the concentrations should be 0.10 M , the make-up concentration of H_3PO_4 . The fact that the sum, $0.08 + 0.024 = 0.104 \text{ M}$, does not equal the total added initially is due to the number of significant figures; i.e., the final digit in the sum is not significant.

6.5-5. Hydrogen Sulfide Exercise

EXERCISE 6.12:

A saturated solution of hydrogen sulfide is 0.10 M at 1 atm and $25 \text{ }^\circ\text{C}$. What are the concentrations of all species present in a saturated H_2S solution? ($K_1 = 1.0\text{e-}7$ and $K_2 = 1.3\text{e-}13$.)

First, determine the concentrations of the species involved in the first reaction. Use "x" as the unknown identifier, and assume that it is negligible compared to 0.10 M on the "eq" line.

	H_2S	+	H_2O	\rightleftharpoons	HS^{1-}	+	H_3O^{1+}	$K_1 = 1.0\text{e-}07$
initial								M
Δ								M
eq								M

$[\text{HS}^{1-}] = \text{_____} \text{ M}$

$[\text{H}_3\text{O}^{1+}] = \text{_____} \text{ M}$

$[\text{H}_2\text{S}] = \text{_____} \text{ M}$

Next, determine the concentration of the species formed in the second reaction. Use "y" as the unknown identifier, and assume it is negligible on the "eq" line.

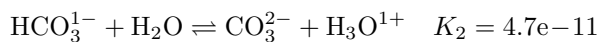
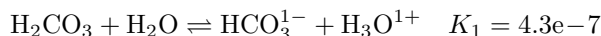
	HS^{1-}	+	H_2O	\rightleftharpoons	S^{2-}	+	H_3O^{1+}	$K_2 = 1.3\text{e-}13$
initial								M
Δ								M
eq								M

$[\text{S}^{2-}] = \text{_____} \text{ M}$

6.5-6. Carbonic Acid Exercise

EXERCISE 6.13:

Determine the pH and the concentrations of all carbon containing species in 0.18 M H₂CO₃ solution.



$$[\text{H}_2\text{CO}_3] = \text{_____ } M \quad \text{pH} = \text{_____}$$

$$[\text{HCO}_3^{1-}] = \text{_____ } M \quad [\text{CO}_3^{2-}] = \text{_____ } M$$

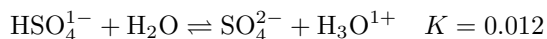
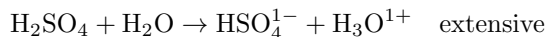
$$[\text{H}_3\text{O}^{1+}] = \text{_____ } M$$

6.5-7. Sulfuric Acid Exercise

EXERCISE 6.14:

What are the H₃O¹⁺, HSO₄¹⁻, and SO₄²⁻ concentrations in 0.10 M sulfuric acid?

Sulfuric acid is a strong acid and its conjugate base (hydrogen sulfate ion) is one of the strongest weak acids, so this exercise is a little different.



After the extensive deprotonation of H₂SO₄:

$$[\text{H}_3\text{O}^{1+}] = \text{_____ } M \quad [\text{HSO}_4^{1-}] = \text{_____ } M$$

Assume the amount of HSO₄¹⁻ that reacts in the second step is negligible.

$$[\text{SO}_4^{2-}] = \text{_____ } M$$

However, that would require a 12% reaction, so the amount that reacts is not negligible. Use the quadratic formula to obtain the equilibrium concentrations.

$$[\text{SO}_4^{2-}] = \text{_____ } M \quad [\text{H}_3\text{O}^{1+}] = \text{_____ } M$$

$$[\text{HSO}_4^{1-}] = \text{_____ } M$$

6.6 Strong Bases

Introduction

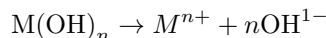
The solutions of strong bases are usually made by dissolving metal hydroxides in water. In this section, we discuss how the pH of a strong base solution is determined.

Objective

- Calculate the pH of the solutions of strong bases.

6.6-1. Strong Base Solutions

Dissolving a metal hydroxide in water is represented by the following chemical equation.



$[OH^{1-}] = nc_o$ in such a solution. However, most metal hydroxides are only sparingly soluble, so the metal is normally a Group 1 metal ion ($n = 1$) or Ba^{2+} ($n = 2$) in solutions with appreciable hydroxide ion concentrations.

6.6-2. Exercise

EXERCISE 6.15:

What is the pH of a solution labeled 0.16 M $Ba(OH)_2$ at 25 °C? pH cannot be determined directly for a base, so we can either convert the hydroxide ion concentration to a hydronium concentration and then determine the pH, or we can convert the hydroxide ion concentration to a pOH and then to a pH. We choose the latter.

$$OH^{1-} = \text{_____} M \qquad \qquad \qquad pH = \text{_____}$$

$$pOH = \text{_____}$$

6.7 Weak Bases

Introduction

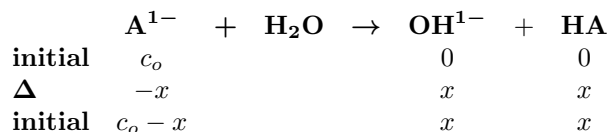
Weak bases are treated in a manner identical to that used for weak acids.

Objectives

- Write the K_b expression for a weak base.
- Determine the equilibrium concentrations of all species present in and the pH of solutions of weak bases.
- Determine the pH, K_b , or initial concentration of a weak base solution given the other two.
- Convert between pK_b and K_b .
- Convert between the K_a and K_b of a conjugate acid-base pair.

6.7-1. Weak Base-Water Reaction

The equilibrium constant for the reaction of a base and water has the symbol, K_b . K_b is small for weak bases, so only a portion of a weak base reacts with water. Thus, the Δ line entries of the reaction table are unknown. Consider the reaction of a generic weak base A^{1-} with water.



Water is the solvent, so it is treated as a pure liquid (activity = 1), so the K_b expression is the following.

$$K_b = \frac{[OH^{1-}][HA]}{A^{1-}} = \frac{(x)(x)}{c_o - x} \qquad \text{Weak Base Equilibrium Constant} \qquad (6.8)$$

If we assume that the extent of reaction of the weak base is negligible, i.e., $c_o - x = c_o$, we can express the K_b expression as follows.

$$K_b = \frac{x^2}{c_o}$$

which can be solved for x , the concentration of the hydroxide ion or the conjugate acid (HA).

$$[\text{OH}^{-1}] = [\text{HA}] = \sqrt{K_b c_o} \quad \text{Solving the } K_b \text{ Expression} \quad (6.9)$$

6.7-2. Relating K_a and K_b

Consider the product of the K_a of HA (a weak acid) and the K_b of A^{1-} (its conjugate base).

$$(K_a)(K_b) = \frac{[\text{H}_3\text{O}^{1+}][\text{A}^{1-}]}{[\text{HA}]} \times \frac{[\text{OH}^{1-}][\text{HA}]}{[\text{A}^{1-}]}$$

Note that $[\text{A}^{1-}]$ appears in the numerator of K_a and in the denominator of K_b , so the two terms cancel. Similarly, $[\text{HA}]$ appears in the denominator of K_a and in the numerator of K_b , so these two terms cancel as well. Canceling these terms results in the following.

$$(K_a)(K_b) = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]$$

Substitution of K_w for $[\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]$ produces Equation 6.10.

$$K_a K_b = K_w \quad \text{Relating } K_a \text{ and } K_b \text{ of a Conjugate Acid-Base Pair} \quad (6.10)$$

The Acid-Base Table with $\text{p}K_a$ gives only K_a and $\text{p}K_a$, so Equation 6.10 must be used to determine the K_b of the conjugate base. At 25 °C, $K_w = 1.0 \times 10^{-14}$, so the following can be used to determine the K_b at 25 °C.

$$K_b = \frac{1.0 \times 10^{-14}}{K_a} \quad K_b \text{ from } K_a \text{ at } 25 \text{ }^\circ\text{C} \quad (6.11)$$

6.7-3. Weak Base pH Exercise

EXERCISE 6.16:

What is the pH of a solution that is 0.12 M in NO_2^{1-} ? (The relevant $\text{p}K_a$ can be found in the Acid-Base Table with $\text{p}K_a$.)

$$K_b = \underline{\hspace{2cm}}$$

$$\text{pOH} = \underline{\hspace{2cm}}$$

$$[\text{OH}^{-1}] = \underline{\hspace{2cm}} \text{ M}$$

$$\text{pH} = \underline{\hspace{2cm}}$$

6.7-4. $\text{p}K_a$ and $\text{p}K_b$

Acid and base constants are frequently given on the p-scale as follows.

$$\begin{aligned} \text{p}K_a &= -\log(K_a) \\ \text{p}K_b &= -\log(K_b) \end{aligned} \quad \text{p}K_a \text{ and } \text{p}K_b \text{ Definitions} \quad (6.12)$$

Due to the minus sign in the definition, a higher $\text{p}K_a$ or $\text{p}K_b$ indicates a weaker acid or base. Taking the negative logarithm of both sides of Equation 6.10 produces the following relationship.

$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00 \text{ at } 25 \text{ }^\circ\text{C} \quad \text{p}K_a \text{ and } \text{p}K_b \text{ Relationship} \quad (6.13)$$

6.7-5. Determining K_b Exercise

EXERCISE 6.17:

The pH of a 0.085- M solution of methylamine is 11.77. What are the K_b of methylamine (CH_3NH_2) and the pK_a of $\text{CH}_3\text{NH}_3^{1+}$, its conjugate acid?

$$[\text{OH}^{1-}] = \text{_____ } M$$

$$K_b = \text{_____}$$

$$[\text{CH}_3\text{NH}_3^{1+}] = \text{_____ } M$$

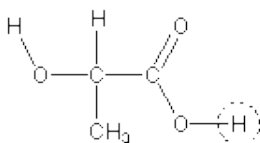
$$pK_a \text{ of } \text{CH}_3\text{NH}_3^{1+} = \text{_____}$$

$$[\text{CH}_3\text{NH}_2] = \text{_____ } M$$

6.7-6. pK_a , pK_b , K_a , and K_b Exercise

EXERCISE 6.18:

Lactic acid is usually prepared by fermentation of starch, cane sugar, or whey. Large amounts of lactic acid in muscle lead to fatigue and can cause cramps. Lactic acid, generated in milk by fermentation of lactose, causes milk to sour. Lactic acid is used in the preparation of cheese, soft drinks, and other food products. Its structure is given below. The proton with a circle around it is the acidic proton.



The pK_a of lactic acid is 3.89.

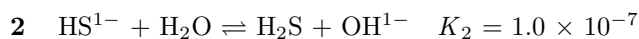
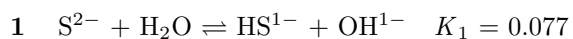
$$K_a \text{ of lactic acid} = \text{_____}$$

$$K_b \text{ of lactate ion} = \text{_____}$$

$$pK_b \text{ of lactate ion} = \text{_____}$$

6.7-7. Bases of Polyprotic Acids

Bases that can accept more than one proton are treated much the same way as polyprotic acids. Consider the case of the sulfide ion, which can accept two protons.



Note that the two K_b values differ by a factor of about a million. Thus, the hydroxide produced in the second step is negligible compared to that produced in the first step. Consequently, the hydroxide ion concentration in an aqueous solution of a base that can accept more than one proton can usually be determined by considering only the first step.

6.7-8. Base of a Polyprotic Acid Exercise

EXERCISE 6.19:

What is the pH of 0.064 M sulfide ion? (The relevant pK_a can be found in the Acid-Base Table with pK_a .)

$$K_b = \underline{\hspace{2cm}}$$

$$[\text{OH}^{1-}] = \underline{\hspace{2cm}} \text{ using Equation 6.9. Check 5\% assumption.}$$

$$[\text{OH}^{1-}] = \underline{\hspace{2cm}} \text{ using quadratic formula if assumption is not valid.}$$

$$\text{pOH} = \underline{\hspace{2cm}}$$

$$\text{pH} = \underline{\hspace{2cm}}$$

6.8 Salts of Weak Acids and Bases

Introduction

Salts are ionic compounds that are produced in acid-base reactions. The anion of the salt is the conjugate base of the reacting acid, and the cation is usually a metal ion that was associated with the reacting base. For example, the reaction between NaOH and HCl is the acid-base reaction between H_3O^{1+} and OH^{1-} . Na^{1+} ion, the metal ion associated with the reacting base and Cl^{1-} , the conjugate base of the reacting acid serve as spectator ions. Combination of the spectator ions produces a salt, NaCl. Salts can be acidic, basic, or neutral depending upon the relative acidity/basicity of the cation and anion. In this section, we discuss the acid-base properties of salts.

Objective

- Define the term salt and predict whether a salt is neutral, basic, or acidic.

6.8-1. Acid-Base Properties of Cations and Anions

Small, highly-charged metal cations have orbitals available to accept electron pairs to form covalent bonds, so they are Lewis acidic. However, the available orbitals of the 1A metal ions are so high in energy that these ions are not acidic in aqueous solutions. Thus, 1A metal ions do not impact the acidity or basicity of a salt. For simplicity, we will limit our use of metal ions to 1A metal ions. The only other common cation is NH_4^{1+} , which is acidic.

Most anions readily accept the positive charge of a proton, so anions are usually good bases. The exceptions are the conjugate bases of the strong acids (ClO_4^{1-} , Cl^{1-} , Br^{1-} , I^{1-} , and NO_3^{1-}), which are neutral, and the protonated anions (HSO_4^{1-} , HSO_3^{1-} and $\text{H}_2\text{PO}_4^{1-}$), which are acidic.

6.8-2. Acid-Base Properties of Salts

A salt can be acidic, basic, or neutral depending upon the relative acid and base strengths of the cation and anion.

- 1 **Neutral Salts:** The reaction of a strong acid and a strong base produces a neutral salt. The cation in such reactions is a 1A metal and the anion is the conjugate base of a strong acid. Thus, both ions are neutral, which produces a neutral salt. The salt of a weak acid and a weak base can be neutral only when the K_a of the cation equals the K_b of the anion. Ammonium acetate is a neutral salt formed in the reaction of acetic acid and ammonia. It is neutral because the K_a of the ammonium ion equals the K_b of the acetate ion.
- 2 **Basic Salts:** Basic Salts are produced in the reaction between a weak acid and a strong base. For example, NaCN is a basic salt that is produced by the reaction of HCN and NaOH. It is basic because sodium ion does not impact the acid-base properties, while the cyanide ion is a basic anion. Basic salts are produced in the reaction between a weak acid and a weak base if the K_b of the base is greater than the K_a of the acid.

Ammonium sulfide is a basic salt because the K_b of the sulfide ion is greater than the K_a of the ammonium ion. Basic salts are the most common source of weak bases.

- 3 **Acidic salts:** The reaction of a strong acid and a weak base produces acidic salts. NH_4Cl is an acidic salt produced by the reaction between HCl and NH_3 . It is acidic because the ammonium ion is a weak acid, but chloride ion is the conjugate base of a strong acid, so it is not basic. Ammonium fluoride is acidic because the K_a of ammonium ion is greater than the K_b of the fluoride ion.

6.8-3. Predicting Salt Basicity and Acidity Exercise

EXERCISE 6.20:

Indicate whether a solution of each of the following salts is acidic, basic, or neutral.

KClO_4	Na_2S	NH_4NO_2
acidic	acidic	acidic
basic	basic	basic
neutral	neutral	neutral
$(\text{NH}_4)_3\text{PO}_4$	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	
acidic	acidic	
basic	basic	
neutral	neutral	

6.8-4. Determining the pH of a Salt Exercise

EXERCISE 6.21:

What is the pH of a solution prepared by dissolving 3.5 g of KF ($M_m = 58.1 \text{ g}\cdot\text{mol}^{-1}$) in sufficient water to make 150 mL of solution? (The relevant $\text{p}K_a$ can be found in the Acid-Base Table with $\text{p}K_a$.)

$$K_b \text{ for } \text{F}^{1-} = \text{_____} \quad [\text{OH}^{1-}] = \text{_____ } M$$

$$\text{mol } \text{F}^{1-} = \text{_____ mol} \quad \text{pOH} = \text{_____}$$

$$[\text{F}^{1-}] = \text{_____ } M \quad \text{pH} = \text{_____}$$

6.9 Amphiprotic Salts

Introduction

Amphiprotic salts are both acids and bases, so their aqueous equilibria are slightly more complicated than those of weak acids or bases. In this section, we discuss the equilibria and give a simple expression for determining their pH.

Objective

- Determine the pH of a solution of an amphiprotic salt.

6.9-1. Acid Equilibrium

As shown in the figure, HCO_3^{1-} is an amphiprotic substance because it can behave as both an acid and a base.

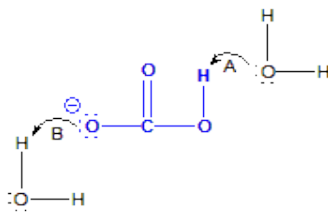
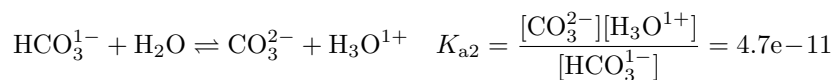


Figure 6.3: Amphoteric Substances are Both Acids and Bases HCO_3^{1-} is amphoteric because its acidic proton can be lost (arrow A) or a lone pair on the oxygen with negative formal charge can accept a proton (arrow B).

It produces hydronium ion through its K_a reaction.

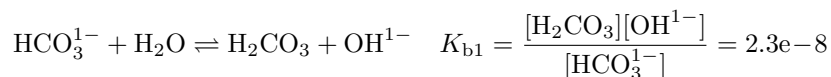


For every mole of hydronium produced, a mole of carbonate ion is also produced; i.e.,

$$[\text{OH}^{1-}]_{\text{produced}} = [\text{CO}_3^{2-}]$$

The concentration of hydronium ion produced in this step equals the equilibrium concentration of its conjugate base, carbonate ion.

However, HCO_3^{1-} also produces hydroxide ion through its K_b reaction.



For every mole of hydroxide ion produced, a mole of carbonic acid is also produced; i.e.,

$$[\text{OH}^{1-}]_{\text{produced}} = [\text{H}_2\text{CO}_3]$$

Each mole of hydroxide ion that is produced consumes a mole of hydronium ion ($\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2 \text{H}_2\text{O}$). Thus, the following is true.

$$[\text{OH}^{1-}]_{\text{produced}} = [\text{H}_3\text{O}^{1+}]_{\text{consumed}} = [\text{H}_2\text{CO}_3]$$

The equilibrium hydronium ion concentration is the following.

$$[\text{H}_3\text{O}^{1+}] = [\text{H}_3\text{O}^{1+}]_{\text{produced}} - [\text{H}_3\text{O}^{1+}]_{\text{consumed}} = [\text{CO}_3^{2-}] - [\text{H}_2\text{CO}_3]$$

The concentrations of CO_3^{2-} and H_2CO_3 can be obtained from K_{a2} and K_{b1} . After some algebra and the assumption that $[\text{HCO}_3^{1-}] \gg K_{a1}$, we arrive at the result below.

$$\text{pH} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) \quad \text{pH of an Amphoteric Salt} \quad (6.13)$$

The pH of an amphoteric substance is half-way between its $\text{p}K_a$ ($\text{p}K_2$) and that of its conjugate acid ($\text{p}K_1$) so long as its concentration is much larger than the K_a of its conjugate acid, K_{a1} .

6.10 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.