

CHAPTER 17: Advanced Acid-Base Equilibria

Chapter In Context

We will now expand the introductory coverage of acid-base equilibria in the previous chapter and explore the chemistry of more complicated aqueous solutions containing acids and bases. First we will address the different types of acid-base reactions and then move on to study buffer solutions, acid-base titrations, and polyprotic acids. So that you can get a feeling for the importance of buffers in your world, we will also briefly discuss the chemistry of two important buffers in biological systems. In the following chapter we will conclude our coverage of chemical equilibria with Lewis acids and bases and the equilibria of sparingly soluble compounds.

One of the more important types of acid-base solutions in terms of commercial and biological applications are buffers because they allow us to control the pH of a solution.

Buffers play an important role wherever you look:

- **Biology:** You are composed of molecules that depend on hydrogen bonding for their structure and function, and are therefore highly sensitive to pH. Most of the reactions in your body occur in aqueous solutions containing buffering agents. It is not surprising that human blood is highly buffered, for if blood is not maintained at a pH near 7.4, death can occur.
- **Industry:** Buffers are important in the syntheses of pharmaceutical chemicals, where the yield and purity of the desired product depends on solution pH. Without buffers, an industrial process for the synthesis of a life-saving drug could yield a product contaminated with a poisonous impurity.
- **In your home:** Take a close look at your shampoo bottle, and you are likely to see the words “pH balanced”. Buffers are a central component in many consumer products, particularly personal hygiene products, where both effectiveness and safety depend on keeping the pH within a narrow range.

Chapter 17

- 17.1 Acid-Base Reactions
- 17.2 Buffers
- 17.3 Acid-Base Titrations
- 17.4 Polyprotic Acids
- 17.5 Two Important Buffer Systems

Chapter Goals

- Recognize the different types of and the extent of acid-base reactions.
- Describe the components of a buffer.
- Apply the principles of acid-base equilibria to buffer solutions.
- Apply the concepts of acid-base equilibria to acid-base titrations.
- Interpret acid-base titration plots.
- Apply the principles of acid-base equilibria to aqueous solutions of polyprotic acids.

1. Acid-Base Reactions



OWL Opening Exploration
17.1 Extent of Acid-Base Reactions: Simulation

In Chapter 5, you learned that acids and bases react to form water and a salt and that these reactions are called neutralization reactions because, on completion of the reaction, the solution is neutral. As shown in Table 17.1, however, acid-base reactions do not always result in the formation of a solution with a neutral pH. There are four classes of acid-base reactions: strong acid + strong base, strong acid + weak base, weak acid + strong base, and weak acid + weak base. For each, we will investigate the extent of reaction and the pH of the resulting solution when equimolar amounts of reactants are combined.

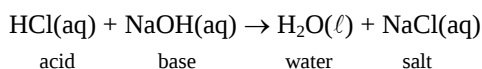
Flashback
5.X Acid-Base Reactions

TABLE 17.1 ACID-BASE REACTIONS

Reaction	Example	pH at Equilibrium
Strong acid + Strong base	$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O}(\ell) + \text{NaCl(aq)}$	7
Strong acid + Weak base	$\text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell) + \text{NH}_4^+(\text{aq})$	< 7
Weak acid + Strong base	$\text{HClO(aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell) + \text{ClO}^-(\text{aq})$	> 7
Weak acid + Weak base	$\text{HClO(aq)} + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{ClO}^-(\text{aq})$	Depends on K_a and K_b

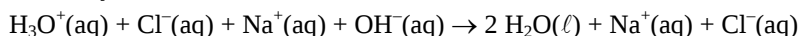
Strong Acid + Strong Base

The reaction between a strong acid and a strong base produces water and a salt (an ionic compound consisting of the cation from the strong base and the anion from the strong acid):

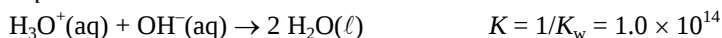


The net ionic equation for any reaction between a strong acid and a strong base is the reverse of the K_w reaction.

Complete ionic equation:



Net ionic equation:

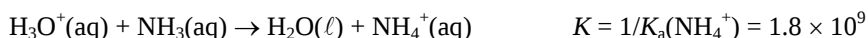


The large value of K for this reaction indicates that in a strong acid + strong base reaction, the reactants are completely consumed to form products. The resulting solution is pH neutral (pH = 7).

Notice that a single arrow ($\rightarrow$) is used to indicate that the reaction goes essentially to completion.

Strong Acid + Weak Base

The reaction between a strong acid and a weak base has a large equilibrium constant and therefore goes essentially to completion. The net ionic equation for the reaction of the strong acid HCl (100% ionized in solution) with the weak base NH_3 is



The extent of reaction can be predicted by recognizing that of the two Brønsted acids in this reaction (H_3O^+ and NH_4^+), the hydronium ion is a much better proton donor (a much stronger acid) so the acid-base reaction favors the formation of the weaker acid, NH_4^+ . In

Flashback
16.5 Acid-Base Properties of Salts



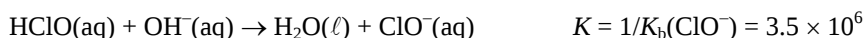
16.29
pH of Salt Solutions

general, all acid-base reactions favor the direction where a stronger acid and base react to form a weaker acid and base.

When the reaction is complete, the solution contains a weak acid, NH_4^+ , and is acidic ($\text{pH} < 7$).

Weak Acid + Strong Base

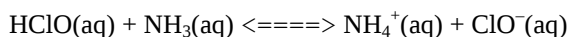
The reaction between a weak acid and a strong base has a large equilibrium constant and therefore goes essentially to completion. The net ionic equation for the reaction of the weak acid HClO with the strong base NaOH (100% ionized in solution) is



In this reaction, HClO is a stronger acid than H_2O (and OH^- is a stronger base than ClO^-) so the reaction favors the formation of products, the weaker acid (H_2O) and base (ClO^-). When the reaction is complete, the solution contains a weak base, ClO^- , and is basic ($\text{pH} > 7$).

Weak Acid + Weak Base

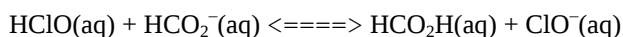
In the reaction between a weak acid and a weak base the magnitude of the equilibrium constant and therefore the extent of reaction depends on the relative strength of the acids and bases in the reaction. The net ionic equation for the reaction of the weak acid HClO with the weak base NH_3 is



In this example, HClO ($K_a = 3.5 \times 10^{-8}$) is a stronger acid than NH_4^+ ($K_a = 5.6 \times 10^{-10}$) so the reaction is product-favored. The reaction does not go essentially to completion, however, so a significant concentration of all four species (along with H_3O^+ and OH^-) is found at equilibrium.

At equilibrium, the pH of the resulting solution depends on acid-base strength of the predominant species in solution, NH_4^+ and ClO^- . In this example, $K_b(\text{ClO}^-) > K_a(\text{NH}_4^+)$, and the solution is basic ($\text{pH} > 7$).

Consider the reaction between the weak acid HClO and the weak base HCO_2^- .



Comparing the relative strength of the bases in this reaction, ClO^- ($K_b = 2.9 \times 10^{-7}$) is a stronger base than HCO_2^- ($K_b = 5.6 \times 10^{-11}$) so the reaction is reactant-favored. Comparing the two predominant species at equilibrium, $K_a(\text{HClO}) > K_b(\text{HCO}_2^-)$ and the solution is acidic ($\text{pH} < 7$).



OWL Concept Exploration
17.2 Relative Strengths and Extent of Reaction

Chapter Goals Revisited

- Recognize the different types of and the extent of acid-base reactions. **Predict if an acid-base reaction is reactant- or product-favored; identify the extent of reaction and the solution pH at equilibrium.**

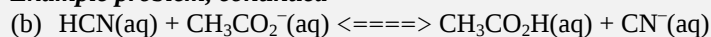
EXAMPLE PROBLEM: Acid-Base Reactions

- Write the net ionic equation for the reaction between nitrous acid and potassium hydroxide. Is the reaction reactant- or product-favored?
- When equimolar amounts of hydrocyanic acid and the acetate ion react, is the reaction reactant- or product-favored? Predict the pH of the solution at equilibrium.

SOLUTION:

- $\text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell) + \text{NO}_2^-(\text{aq})$

HNO_2 is a much stronger acid than H_2O (and OH^- is a much stronger base than NO_2^-). The reaction will favor the formation of the weaker acid and base, so the reaction is product-favored. Reactions between weak acids and strong bases are assumed to be 100% complete.

Example problem, continued

Acetic acid is a stronger acid than hydrocyanic acid (and the cyanide ion is a stronger base than the acetate ion). The equilibrium will favor the weaker acid and base (reactant-favored). The pH of the solution at equilibrium is controlled by the predominant species in solution, HCN and CH_3CO_2^- . The solution is basic because $K_b(\text{CH}_3\text{CO}_2^-) > K_a(\text{HCN})$.



OWL Example Problems
17.3 Acid/Base Reactions

2. Buffer Solutions

OWL Opening Exploration
17.4 Buffer Solutions: Simulation

A **buffer solution** contains a mixture of a weak acid and a weak base, typically the conjugate base of the weak acid. The principle property of a buffer solution is that it experiences a relatively small change in pH when a strong acid or a strong base is added. A common buffer solution used in the lab contains both acetic acid and sodium acetate, the sodium salt of the conjugate base. Some other examples of buffers include 1.00 M KH_2PO_4 and 0.40 M K_2HPO_4 , and 0.24 M NH_4Cl and 0.24 M NH_3 .

Chapter Goals Revisited

- Describe the components of a buffer. **Identify the weak acid and conjugate base components of a buffer.**

EXAMPLE PROBLEM: Identifying Buffer Solutions

Identify buffer solutions from the list below.

- 0.13 M sodium hydroxide + 0.27 M sodium bromide
- 0.13 M nitrous acid + 0.14 M sodium nitrite
- 0.24 M nitric acid + 0.17 M sodium nitrate
- 0.31 M calcium chloride + 0.25 M calcium bromide
- 0.34 M ammonia + 0.38 M ammonium bromide

SOLUTION:

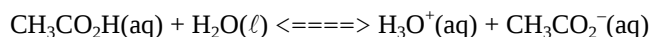
- This is not a buffer. Sodium hydroxide is a strong base and sodium bromide is a neutral salt.
- This is a buffer solution. Nitrous acid is a weak acid and sodium nitrite is a source of its conjugate base, the nitrite ion.
- This is not a buffer. Nitric acid is a strong acid and sodium nitrate is a neutral salt.
- This is not a buffer. Both are neutral salts.
- This is a buffer solution. The ammonium ion (present as ammonium bromide) is a weak acid and ammonia is its conjugate base.



OWL Example Problems
17.5 Identifying Buffer Solutions: Tutor
17.6 Identifying Buffer Solutions

Buffer pH

The **common ion effect**, the resulting shift in an equilibrium that results from adding to a solution a chemical species that is common to an existing equilibrium, helps to understand the pH of buffer solutions. Consider a solution containing the weak acid acetic acid:



The addition of sodium acetate, a source of the weak base CH_3CO_2^- , shifts the equilibrium to the left, suppressing the acid hydrolysis (the forward reaction) and

increasing the pH. The following example problem demonstrates the common ion effect in an acetic acid-sodium acetate buffer solution.



OWL Concept Exploration
17.7 Common Ion Effect: Simulation

Chapter Goals Revisited

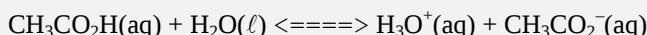
- Apply the principles of acid-base equilibria to buffer solutions.
Calculate the pH of a buffer solution

EXAMPLE PROBLEM: pH of Buffer Solutions (1)

Calculate the pH of 125 mL of a 0.15 M solution of acetic acid before and after the addition of 0.015 mol of sodium acetate.

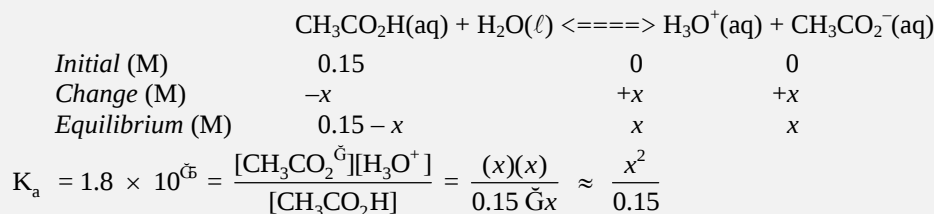
SOLUTION:

Step 1. Write the balanced equation for the acid hydrolysis reaction.



When solving problems involving buffers, it is important to first write the weak acid hydrolysis reaction before considering the effect of added conjugate base.

Step 2. Set up an ICE table and calculate the pH of the weak acid solution (see Section 16.4).

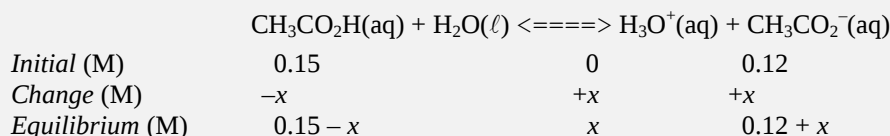


$$x = [\text{H}_3\text{O}^+] = 1.6 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.78$$

Step 3. Set up a new ICE table for the buffer that now includes the concentration of the common ion, the acetate ion.

$$[\text{CH}_3\text{CO}_2^-]_{\text{initial}} = \frac{0.015 \text{ mol CH}_3\text{CO}_2^-}{0.125 \text{ L}} = 0.12 \text{ M}$$



Step 4. Substitute these equilibrium concentrations into the K_a expression.

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(0.12 + x)(x)}{0.15 - x} \approx \frac{(0.12)(x)}{0.15}$$

We can make the assumption that x is small when compared to the initial acid and conjugate base concentrations because (1) K_a is small and (2) the presence of a common ion suppresses the weak acid hydrolysis.

Step 5. Solve the expression for $[\text{H}_3\text{O}^+]$ and calculate pH.

$$x = [\text{H}_3\text{O}^+] = K_a \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} = 1.8 \times 10^{-5} \left(\frac{0.15}{0.12} \right) = 2.3 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.65$$

The pH of the solution has increased (the solution is more basic) because a weak base, the acetate ion, was added to the solution to form a buffer.

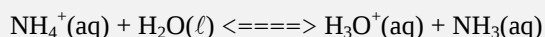
A buffer solution can consist of either a weak acid and its conjugate base or a weak base and its conjugate acid. To be consistent, we will treat all buffers as weak acid systems as shown in the following example.

EXAMPLE PROBLEM: pH of Buffer Solutions (2)

A 0.30 M aqueous solution of NH_3 has a pH of 11.37. Calculate the pH of a buffer solution that is 0.30 M in NH_3 and 0.23 M in ammonium bromide.

SOLUTION:

Step 1. Write the balanced equation for the acid hydrolysis reaction. In this example the weak acid is the ammonium ion.



Step 2. Set up an ICE table for the buffer solution.

	$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$		
Initial (M)	0.23	0	0.30
Change (M)	-x	+x	+x
Equilibrium (M)	$0.23 - x$	x	$0.30 + x$

Step 3. Substitute these equilibrium concentrations into the K_a expression.

$$K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(0.30 + x)(x)}{0.23 - x} \approx \frac{(0.30)(x)}{0.23}$$

Once again, we can make the assumption that x is small when compared to the initial acid and conjugate base concentrations.

Step 4. Solve the expression for $[\text{H}_3\text{O}^+]$ and calculate pH.

$$x = [\text{H}_3\text{O}^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 5.6 \times 10^{-10} \left(\frac{0.23}{0.30} \right) = 4.3 \times 10^{-10} \text{ M}$$

$$\text{pH} = 9.37$$

Addition of a weak acid, ammonium ion, decreases the pH of the solution (the solution is more acidic).



OWL Example Problems

17.8 pH of Buffer Solutions – K_a method

The rearranged K_a expression used in the previous example problems can be used for calculating the pH of any buffer solution. In general for a weak acid/conjugate base buffer,

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{weak acid}]}{[\text{conjugate base}]}$$

We can rewrite this equation in terms of pH and $\text{p}K_a$ by taking the negative logarithm of both sides.

$$-\log[\text{H}_3\text{O}^+] = -\log \left(K_a \frac{[\text{weak acid}]}{[\text{conjugate base}]} \right)$$

$$-\log[\text{H}_3\text{O}^+] = -\log(K_a) + \left(-\log \frac{[\text{weak acid}]}{[\text{conjugate base}]} \right)$$

$$\text{pH} = \text{p}K_a - \log \frac{[\text{weak acid}]}{[\text{conjugate base}]}$$

$$\text{Because } -\log \frac{[\text{weak acid}]}{[\text{conjugate base}]} = +\log \frac{[\text{conjugate base}]}{[\text{weak acid}]},$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} \quad (17.1)$$

Equation 17.1 is known as the **Henderson-Hasselbalch equation**, a very useful form of the K_a expression that is often used to calculate the pH of buffer solutions.

The Henderson-Hasselbalch equation is only used for calculations involving buffer solutions. It is not used if a solution contains only a weak acid or only a weak base.

The Henderson-Hasselbalch equation also shows that the weak acid pK_a has a strong influence on the pH of a buffer, and that buffer pH can be manipulated by changing the ratio of [conjugate base] to [weak acid]. Notice that in the special case where [weak acid] = [conjugate base], the ratio of concentrations is equal to 1 and the pH of the buffer solution is equal to the weak acid pK_a .

$$\text{When } [\text{weak acid}] = [\text{conjugate base}], \text{ pH} = pK_a + \log(1) = pK_a + 0 = pK_a$$

Buffer components are chosen based on the relationship between weak acid pK_a and the target pH for the buffer. For the buffer to be effective, it should contain significant amounts of both weak acid and conjugate base. Effective buffers, those that can best resist pH change upon addition of a strong acid or base, have a [conjugate base] to [weak acid] ratio between 1:10 and 10:1. As shown below, this results in a buffer pH that is approximately equal to the weak acid $pK_a \pm 1$.

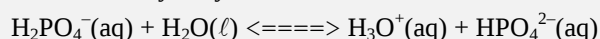
[conjugate base]/[weak acid]	pH of buffer solution
1	$\text{pH} = pK_a$
10/1	$\text{pH} = pK_a + 1$
1/10	$\text{pH} = pK_a - 1$

EXAMPLE PROBLEM: pH of Buffer Solutions (Henderson-Hasselbalch Equation)

Use the Henderson-Hasselbalch equation to calculate the pH of a buffer solution that is 0.18 M in H_2PO_4^- and 0.21 M in HPO_4^{2-} .

SOLUTION:

Step 1. Write the balanced equation for the acid hydrolysis reaction.



Step 2. Set up an ICE table for the buffer solution.

	$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$		
Initial (M)	0.18	0	0.21
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.18 - x$	x	$0.21 + x$

Step 3. Substitute these equilibrium concentrations into the Henderson-Hasselbalch equation and calculate pH.

$$\text{pH} = pK_a + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = -\log(6.2 \times 10^{-8}) + \log \frac{(0.21 + x)}{(0.18 - x)} \approx 7.21 + \log \left(\frac{0.21}{0.18} \right) = 7.27$$

Once again, we can make the assumption that x is small when compared to the initial acid and conjugate base concentrations. Notice that the pH of the buffer solution is greater than pK_a for the weak acid because [conjugate base]/[weak acid] > 1. If the ratio is less than one, $\text{pH} < pK_a$.



OWL Example Problems

17.9 pH of Buffer Solutions: Simulation

17.10 pH of Buffer Solutions (Henderson-Hasselbalch Equation)

Preparing Buffer Solutions

The preparation of a buffer solution with a known pH is a two-step process.

- A weak acid/conjugate base pair is chosen for which the weak acid pK_a is within about 1 pH unit of the desired pH. This guarantees that the [weak acid]:[conjugate base] ratio is between 10:1 and 1:10, ensuring that the solution will contain significant amounts of weak acid and conjugate base and will be able to buffer against the addition of strong acid or base.
- The desired pH and the weak acid pK_a are used to determine the relative concentrations of weak acid and conjugate base needed to give the desired pH.

$\frac{[\text{conj. base}]}{[\text{weak acid}]}$	buffer pH
1	pK_a
10	$pK_a + 1$
1/10	$pK_a - 1$

Once the desired weak acid and conjugate base concentrations are known, the solution is prepared in one of two ways:

- Method 1. Direct addition, where the correct amounts of the weak acid and conjugate base are added to water.
- Method 2. Acid-base reaction, where, for example, a conjugate base is created by reacting a weak acid with enough strong base to produce a solution containing the correct weak acid and conjugate base concentrations.



OWL Concept Exploration
17.11 Preparation of Buffer Solutions: Simulation

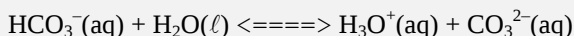
EXAMPLE PROBLEM: Preparation of Buffers by Direct Addition

Describe how to prepare 500. mL of a buffer solution with pH = 9.85 using one of the weak acid/conjugate base systems shown below.

Weak acid	Conjugate base	K_a	pK_a
$\text{CH}_3\text{CO}_2\text{H}$	CH_3CO_2^-	1.8×10^{-5}	4.74
H_2PO_4^-	HPO_4^{2-}	6.2×10^{-8}	7.21
HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32

SOLUTION:

Step 1. Choose a weak acid/conjugate base pair. The bicarbonate ion/carbonate ion buffer system is the best choice here because the desired pH is close to the pK_a of the weak acid. Write the balanced equation for the acid hydrolysis reaction.



Step 2. Determine the necessary weak acid/conjugate base ratio using the rearranged K_a expression for the weak acid. (The Henderson-Hasselbalch equation can also be used to determine the weak acid/conjugate base ratio.)

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.85} = 1.4 \times 10^{-10} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 1.4 \times 10^{-10} = K_a \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = (4.8 \times 10^{-11}) \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$$

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{2.9 \text{ mol/L}}{1.0 \text{ mol/L}} = \frac{2.9 \text{ mol HCO}_3^-}{1.0 \text{ mol CO}_3^{2-}}$$

Notice that the volume of buffer is cancelled in the ratio. The required amounts of weak acid and conjugate base are independent of the solution volume, so *the volume of a buffer has no effect on the buffer pH.*

Step 3. Determine the amount of weak acid and conjugate base that must be combined to produce the buffer solution. Mixing 2.9 mol of HCO_3^- and 1.0 mol of CO_3^{2-} (or any multiple of this ratio) will result in a buffer with a pH of 9.85. Alternately, assuming that each is present in the form of a sodium salt, combine 240 g of NaHCO_3 and 110 g Na_2CO_3 in a flask and add water (to a total volume of 500 mL) to make the buffer solution.

$$2.9 \text{ mol NaHCO}_3 \cdot \frac{84.0 \text{ g}}{1 \text{ mol NaHCO}_3} = 240 \text{ g NaHCO}_3$$

$$1.0 \text{ mol Na}_2\text{CO}_3 \cdot \frac{106 \text{ g}}{1 \text{ mol Na}_2\text{CO}_3} = 110 \text{ g Na}_2\text{CO}_3$$



OWL Example Problems
17.12 Preparation of Buffers by Direct Addition: Tutor
17.12a Preparation of Buffers by Direct Addition

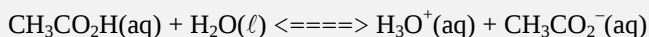
EXAMPLE PROBLEM: Preparation of a Buffers by Acid-base Reactions

Describe how to prepare a buffer solution with pH = 5.25 (using one of the weak acid/conjugate base systems shown below) by combining a 0.50 M solution of weak acid with any necessary amount of 1.00 M NaOH.

Weak acid	Conjugate base	K_a	pK_a
$\text{CH}_3\text{CO}_2\text{H}$	CH_3CO_2^-	1.8×10^{-5}	4.74
H_2PO_4^-	HPO_4^{2-}	6.2×10^{-8}	7.21
HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32

SOLUTION:

Step 1. Choose a weak acid/conjugate base pair. The acetic acid/acetate ion buffer system is the best choice here because the desired pH is close to the pK_a of the weak acid. Write the balanced equation for the acid hydrolysis reaction.



Step 2. Determine the necessary weak acid/conjugate base ratio using the rearranged K_a expression for the weak acid. (The Henderson-Hasselbalch equation can also be used to determine the weak acid/conjugate base ratio.)

$$[\text{H}_3\text{O}^+] = 10^{-5.25} = 5.6 \times 10^{-6} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 5.6 \times 10^{-6} = K_a \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} = (1.8 \times 10^{-5}) \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]}$$

$$\frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} = \frac{0.31 \text{ mol/L}}{1.0 \text{ mol/L}} = \frac{0.31 \text{ mol CH}_3\text{CO}_2\text{H}}{1.0 \text{ mol CH}_3\text{CO}_2^-}$$

Notice that volume units (L) are cancelled in the $\frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]}$ ratio. The required amounts of weak acid and conjugate base are independent of the total solution volume, so the volume of a buffer has no effect on the buffer pH.

Step 3. Determine the amount of weak acid and strong base that must be combined to produce the buffer. Recall that a strong base will react completely with a weak acid forming water and the conjugate base of the weak acid. In this case, the weak acid and strong base react in a 1:1 stoichiometric ratio, so

Initial amount of weak acid required = amount of weak acid in buffer + amount of conjugate base in buffer

$$\text{Initial amount of weak acid required} = 0.31 \text{ mol} + 1.0 \text{ mol} = 1.31 \text{ mol CH}_3\text{CO}_2\text{H}$$

The amount of strong base required is determined by the reaction stoichiometry. Set up a stoichiometry table that shows the amount (mol) of species initially in the solution, the change in amounts of reactants and products (based on the amount of limiting reactant), and the amounts of reactants and products present after the acid-base reaction is complete. In this case, the stoichiometry table is used to determine the initial amount of reactants needed to produce a buffer containing 0.31 mol acetic acid and 1.00 mol acetate ion.

	$\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell) + \text{CH}_3\text{CO}_2^-(\text{aq})$		
Initial (mol)	1.31	1.00	0
Change (mol)	-1.00	-1.00	+1.00
After reaction (mol)	0.31	0	1.00

The combination of 1.31 mol $\text{CH}_3\text{CO}_2\text{H}$ with 1.00 mol OH^- (as NaOH) will produce the buffer solution.

Step 4. Determine the volume of weak acid and strong base solutions that must be combined to produce the buffer solution.

$$1.31 \text{ mol CH}_3\text{CO}_2\text{H} \cdot \frac{1.0 \text{ L}}{0.50 \text{ mol CH}_3\text{CO}_2\text{H}} = 2.6 \text{ L CH}_3\text{CO}_2\text{H solution}$$

$$1.00 \text{ mol NaOH} \cdot \frac{1.0 \text{ L}}{1.00 \text{ mol NaOH}} = 1.00 \text{ L NaOH solution}$$

Mix 2.6 L of 0.50 M $\text{CH}_3\text{CO}_2\text{H}$ with 1.00 L of 1.00 M NaOH to produce a buffer with a pH of 5.25. Note that any ratio of these volumes will produce the buffer with a pH of 5.25. For example, combining 1.0 L of 0.50 M $\text{CH}_3\text{CO}_2\text{H}$ with 0.38 L of 1.00 M NaOH also produces a buffer with a pH of 5.25.



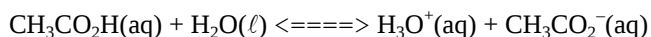
OWL Example Problems

17.13 Preparation of Buffers by Acid-base Reactions: Tutor

17.14 Preparation of Buffers by Acid-Base Reactions

Buffers and pH - Alpha Plots

As shown in the preceding example problems, the pH of a buffer solution is controlled by the relative amounts of weak acid and conjugate base present and by the weak acid pK_a . Regardless of the amounts of weak acid and conjugate base that are present in the solution, the relative amounts can change if the pH is changed by external agents such as a strong acid or a strong base. Consider the acetic acid-acetate ion buffer system:



At very low pH (high $[\text{H}_3\text{O}^+]$) the equilibrium system is shifted to the left and $[\text{CH}_3\text{CO}_2\text{H}] \gg [\text{CH}_3\text{CO}_2^-]$. At very high pH (low $[\text{H}_3\text{O}^+]$) the equilibrium system shifts towards the right and $[\text{CH}_3\text{CO}_2^-] \gg [\text{CH}_3\text{CO}_2\text{H}]$.

This relationship between pH and solution composition is shown graphically in an **alpha plot**, a plot of solution composition (α) versus pH. Alpha is equal to the mol fraction of the acid or base component of the buffer. For an acetic acid-acetate ion alpha plot, for example,

$$\alpha_{\text{CH}_3\text{CO}_2\text{H}} = \frac{\text{mol CH}_3\text{CO}_2\text{H}}{\text{mol CH}_3\text{CO}_2\text{H} + \text{mol CH}_3\text{CO}_2^-} \quad \alpha_{\text{CH}_3\text{CO}_2^-} = \frac{\text{mol CH}_3\text{CO}_2^-}{\text{mol CH}_3\text{CO}_2\text{H} + \text{mol CH}_3\text{CO}_2^-}$$

The alpha plot for the acetic acid-acetate ion buffer system shown below (Figure 17.X) has the following features:

- When the solution pH is more than about 2 pH units below pK_a (4.74) the solution consists of almost all weak acid and almost no conjugate base.
- When the solution pH is more than about 2 pH units above pK_a (4.74) the solution consists of almost all conjugate base and almost no weak acid.
- When the solution pH is near pK_a the solution contains a significant concentration of both weak acid and conjugate base.
- When the solution pH is equal to pK_a the solution is composed of equal parts weak acid and weak base ($\alpha = 0.5$).

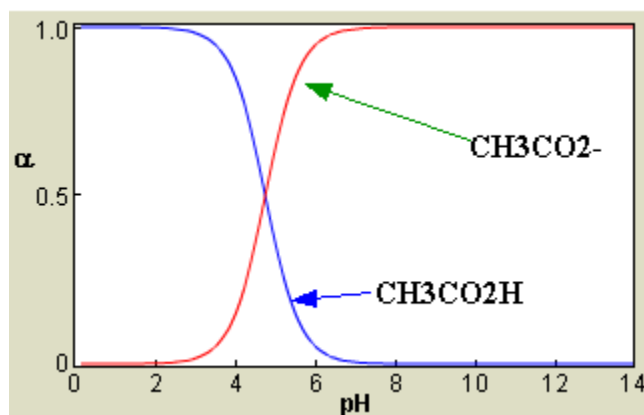


Figure 17.X Acetic acid-acetate ion alpha plot

Buffer pH is independent of solution volume. If a buffer solution is diluted, the pH does not change

Alpha plots will be linked to bullets (color-coded, numbered, etc.)

The ammonia-ammonium ion alpha plot (Figure 17.X) shows that equal amounts of weak acid and conjugate base are found when the pH is equal to the ammonium ion pK_a (9.26).

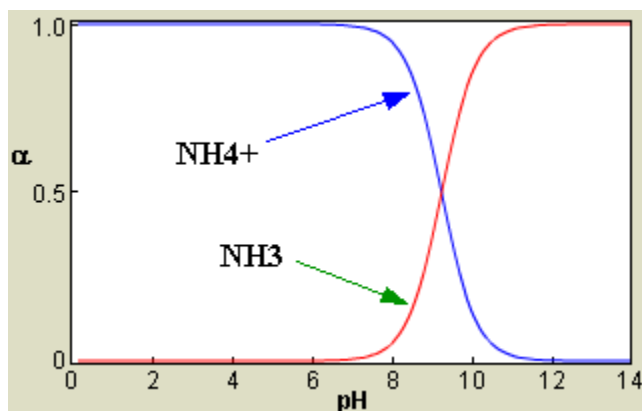


Figure 17.X Ammonium ion-ammonia alpha plot



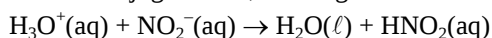
OWL Concept Exploration
17.X Alpha plots

How Does a Buffer Work?

The weak acid and conjugate base components of a buffer make it possible for buffer solutions to absorb strong acid or strong base without a significant pH change.

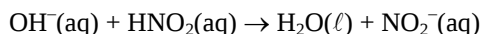
- When a strong acid is added to a buffer it reacts with the conjugate base and is completely consumed. Despite the addition of a strong acid, the pH of the buffer solution decreases only slightly.

Example: When H_3O^+ is added to a nitrous acid-sodium nitrite buffer it consumes some of the conjugate base, forming additional nitrous acid.



- When a strong base is added to a buffer it reacts with the weak acid and is completely consumed. Despite the addition of a strong base, the pH of the buffer solution increases only slightly.

Example: When OH^- is added to a nitrous acid-sodium nitrite buffer it consumes some of the weak acid, forming additional nitrite ion.



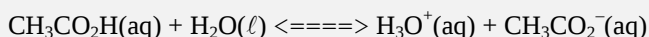
It is a common misconception that buffer pH remains constant when some strong acid or base is added. This is not the case. As shown in the following example, a buffer minimizes the pH change upon addition of strong acid or base because only the weak acid/conjugate base ratio of the buffer is affected. The pH changes, but only by a small amount.

EXAMPLE PROBLEM: Adding Reagents to Buffer Solutions

Determine the pH change when 0.020 mol HCl is added to 1.00 L of a buffer solution that is 0.10 M in $\text{CH}_3\text{CO}_2\text{H}$ and 0.25 M in CH_3CO_2^- .

SOLUTION:

Step 1. Write the balanced equation for the acid hydrolysis reaction.



Step 2. Use the Henderson-Hasselbalch equation to calculate the pH of the buffer solution before the addition of HCl.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = -\log(1.8 \times 10^{-5}) + \log \left(\frac{0.25}{0.10} \right) = 5.14$$

Example problem, continued

Step 3. Assume that the strong acid reacts completely with the conjugate base. Set up a stoichiometry table that shows the amount (mol) of species initially in the solution, the change in amounts of reactants and products (based on the amount of limiting reactant), and the amounts of reactants and products present after the acid-base reaction is complete.

	$\text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell) + \text{CH}_3\text{CO}_2\text{H}(\text{aq})$		
Initial (mol)	0.020	0.25	0.10
Change (mol)	-0.020	-0.020	+0.020
After reaction (mol)	0	0.23	0.12

Step 4. Use the new weak acid and conjugate base concentrations to calculate the buffer pH after adding strong acid.

$$[\text{CH}_3\text{CO}_2\text{H}] = \frac{0.12 \text{ mol}}{1.00 \text{ L}} = 0.12 \text{ M} \quad [\text{CH}_3\text{CO}_2^-] = \frac{0.23 \text{ mol}}{1.00 \text{ L}} = 0.23 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.23}{0.12}\right) = 5.03$$

$$\Delta\text{pH} = 5.03 - 5.14 = -0.11$$

Addition of 0.020 mol of HCl to the buffer decreases the pH only slightly, by 0.11 pH units. If the same amount of HCl is added to 1.00 L of water, the pH decreases by 5.30 pH units, from a pH of 7.00 to a pH of 1.70.

**OWL Example Problems**

17.16 Adding Reagents to Buffer Solutions: Tutor

17.17 Buffer + Acid/Base – Qualitative

17.18 Buffer + Acid/Base – Calculation

3. Acid-Base Titrations**OWL Opening Exploration**

17.19 Titration Plots (Simulation)

As you learned in Chapter 5, an acid-base titration is when one reactant with a known concentration is placed in a buret and is added to the other reactant (of unknown concentration). The progress of the reaction is monitored externally using an acid-base indicator, and the titration endpoint is used to calculate the unknown concentration. We will now consider how pH changes during acid-base titrations involving strong and weak acids and bases. We will construct pH titration plots (a plot of solution pH versus volume of added titrant) that reveal information about the nature of the acid or base under study, the equivalence point in the reaction, and, for weak acids and bases, the weak acid K_a (or weak base K_b).

Strong Acid-Strong Base Titration

In the pH plot for the titration of 75.0 mL of 0.100 M HCl with 0.100 M NaOH (Figure 17.X), there are four distinct regions:

1. The initial pH is less than 7 due to the presence of an acid.
2. The pH rises slowly with the addition of strong base as the base is completely consumed and a pH-neutral salt is formed.
3. Near the equivalence point, where the acid is completely consumed by added base, the pH increases rapidly. The midpoint of this vertical section of the plot (where the pH is 7.00) is the equivalence point of the titration.
4. After the equivalence point the pH is high and increases slowly as excess base is added.

The pH plot for a strong base-strong acid titration (Figure 17.X) has a similar shape but differs in the pH before and after the equivalence point:

Flashback

5.X Solution Stoichiometry

Chapter Goals Revisited

- Apply the concepts of acid-base equilibria to acid-base titrations.
Calculate the pH and pH at various points in an acid-base titration

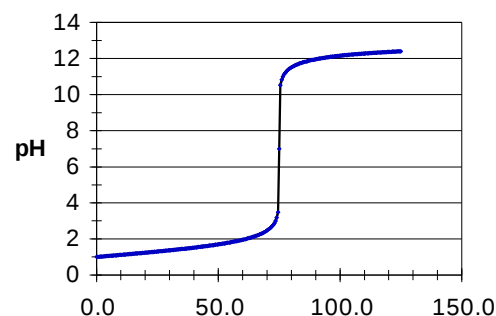


Figure 17.X Strong acid-strong base pH titration plot

1. The initial pH is greater than 7 due to the presence of a base.
2. The pH decreases slowly with the addition of strong acid as the acid is completely consumed and a pH-neutral salt is formed.
3. Near the equivalence point, where the base is completely consumed by added acid, the pH decreases rapidly. The midpoint of this vertical section of the plot (where the pH is 7.00) is the equivalence point of the titration.
4. After the equivalence point the pH is low and decreases slowly as excess acid is added.

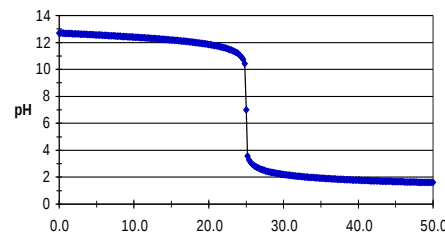


Figure 17.X Strong base-strong acid pH titration plot

The solution pH at four points of a strong acid-strong base titration is calculated in the following example.

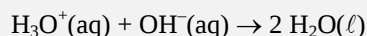
EXAMPLE PROBLEM: Titration of a Strong Acid By a Strong Base

Determine the pH during the titration of 75.0 mL of 0.100 M HCl by 0.100 M NaOH at the following points.

- (a) Before the addition of any NaOH
- (b) After adding 20.0 mL of NaOH
- (c) At the equivalence point
- (d) After adding 100.0 mL of NaOH

SOLUTION:

Write the balanced net ionic equation for the acid-base reaction.



- (a) Calculate the pH of the solution before adding NaOH. HCl is a strong acid and is 100% dissociated in solution, so $[\text{H}_3\text{O}^+] = [\text{HCl}] = 0.100 \text{ M}$.

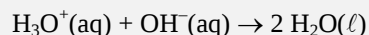
$$\text{pH} = -\log(0.100) = 1.000$$

- (b) Before the equivalence point, all NaOH is consumed by excess HCl. Set up a stoichiometry table.

$$\text{mol H}_3\text{O}^+ = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol H}_3\text{O}^+$$

$$\text{mol OH}^- = (0.0200 \text{ L})(0.100 \text{ mol/L}) = 0.00200 \text{ mol OH}^-$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 20.0 \text{ mL} = 95.0 \text{ mL}$$



<i>Initial (mol)</i>	0.00750	0.00200
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<i>Change (mol)</i>	-0.00200	-0.00200
---------------------	----------	----------

<i>After reaction (mol)</i>	0.00550	0
-----------------------------	---------	---

$$\text{Concentration after reaction (M)} \quad [\text{H}_3\text{O}^+] = \frac{0.00550 \text{ mol}}{0.0950 \text{ L}} = 0.0579 \text{ M}$$

$$\text{pH} = -\log(0.0579) = 1.237$$

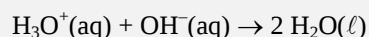
- (c) The equivalence point is reached when 75.0 mL of NaOH is added to the HCl. All base and acid is consumed, forming the pH-neutral salt NaCl and water. At this point, $[\text{H}_3\text{O}^+] = 1.00 \times 10^{-7} \text{ M}$ and **pH = 7.000**.

- (d) After the equivalence point, all HCl has been consumed and the solution contains excess NaOH. Set up a stoichiometry table.

$$\text{mol H}_3\text{O}^+ = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol H}_3\text{O}^+$$

$$\text{mol OH}^- = (0.1000 \text{ L})(0.100 \text{ mol/L}) = 0.0100 \text{ mol OH}^-$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 100.0 \text{ mL} = 175.0 \text{ mL}$$



<i>Initial (mol)</i>	0.00750	0.0100
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Change (mol)	-0.00750	-0.00750
After reaction (mol)	0	0.0025
Concentration after reaction (M)[OH ⁻] = $\frac{0.0025 \text{ mol}}{0.1750 \text{ L}} = 0.014 \text{ M}$		
pOH = $-\log(0.014) = 1.85$		
pH = $14.000 - 1.85 = 12.15$		



OWL Example Problems
17.20 Strong Acid-Strong Base Titration

Weak Acid-Strong Base Titration

The pH titration plot for a weak acid-strong base titration (Figure 17.X) is somewhat different than a strong acid-strong base pH titration plot. There is a significant rise in pH after the initial pH point and then a more gradual increase in pH up to the equivalence point (this region in a strong acid-strong base titration plot is relatively flat) and the equivalence point pH is greater than 7 (the equivalence point in a strong acid-strong base titration plot is equal to 7).

There are four regions of interest in the weak acid-strong base pH plot for the titration of 75.0 mL of 0.100 M benzoic acid ($K_a = 6.3 \times 10^{-5}$) with 0.100 M NaOH:

1. The initial pH is less than 7 because the solution contains an acid.
2. As the strong base is added, the pH rises sharply and then increases gradually until the equivalence point is reached. This is the buffer region of the titration, where the solution contains a weak acid and its conjugate base. At the midpoint of this region, half of the acid originally present in the flask has been consumed and the **half-equivalence point**, also called the titration midpoint, is reached. As shown in the example problem that follows, at this point in the titration the solution pH is equal to the weak acid pK_a .
3. Near the equivalence point, where the acid is completely consumed by added base, the pH increases rapidly. The equivalence point of the titration has a pH greater than 7 due to the presence of the benzoate ion, a basic anion.
4. After the equivalence point the pH is high because it contains excess strong base.

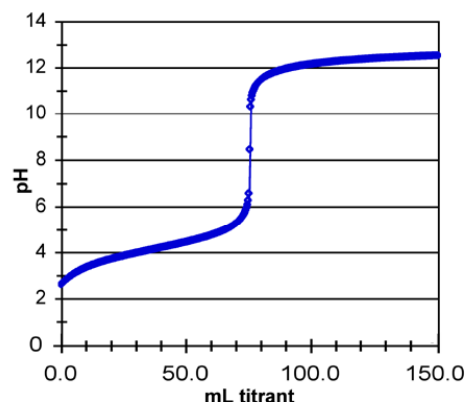


Figure 17.X Weak acid-strong base pH titration plot

The pH of the solution is calculated at five points of the titration in the following example.

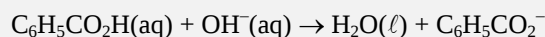
EXAMPLE PROBLEM: Weak Acid-Strong Base Titration

Determine the pH during the titration of 75.0 mL of 0.100 M benzoic acid ($K_a = 6.3 \times 10^{-5}$) by 0.100 M NaOH at the following points.

- (a) Before the addition of any NaOH
- (b) After adding 20.0 mL of NaOH
- (c) At the half-equivalence point (the titration midpoint)
- (d) At the equivalence point
- (e) After adding 100.0 mL of NaOH

SOLUTION:

Write the balanced net ionic equation for the acid-base reaction.



- (a) Calculate the pH of the solution before adding NaOH. Benzoic acid is a weak acid and the pH of the solution is calculated using methods introduced in Section 16.4

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times [\text{C}_6\text{H}_5\text{CO}_2\text{H}]_0} = \sqrt{(6.3 \times 10^{-5})(0.100)} = 0.00251 \text{ M}$$

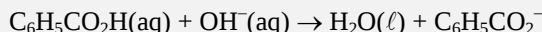
$$\text{pH} = -\log(0.00251) = 2.600$$

- (b) Before the equivalence point, all NaOH is consumed by excess weak acid. First consider the stoichiometry of the acid-base reaction, and then treat the solution as a buffer to calculate pH.

$$\text{mol CH}_3\text{CO}_2\text{H} = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol CH}_3\text{CO}_2\text{H}$$

$$\text{mol OH}^- = (0.0200 \text{ L})(0.100 \text{ mol/L}) = 0.00200 \text{ mol OH}^-$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 20.0 \text{ mL} = 95.0 \text{ mL}$$



Initial (mol)	0.00750	0.00200	0
Change (mol)	-0.00200	-0.00200	+0.00200
After reaction (mol)	0.00550	0	0.00200
Concentration after reaction (M)	$\frac{0.00550 \text{ mol}}{0.0950 \text{ L}} = 0.0579 \text{ M}$		$\frac{0.00200 \text{ mol}}{0.0950 \text{ L}} = 0.0211 \text{ M}$

Use the rearranged K_a expression (or the Henderson-Hasselbalch equation) to calculate pH.

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{C}_6\text{H}_5\text{CO}_2\text{H}]}{[\text{C}_6\text{H}_5\text{CO}_2^-]} = 6.3 \times 10^{-5} \left(\frac{0.0579}{0.0211} \right) = 1.7 \times 10^{-4} \text{ M}$$

$$\text{pH} = 3.76$$

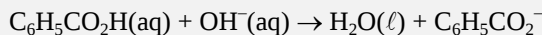
Example problem, continued

- (c) The half-equivalence point, the titration midpoint, is reached when half the amount of strong base required to reach the equivalence point has been added to the weak acid solution and, as a result, half of the weak acid originally in the flask has been consumed. In this example the midpoint in the titration is when 37.5 mL of NaOH is added to the solution.

$$\text{mol CH}_3\text{CO}_2\text{H} = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol CH}_3\text{CO}_2\text{H}$$

$$\text{mol OH}^- = (0.0375 \text{ L})(0.100 \text{ mol/L}) = 0.00375 \text{ mol OH}^-$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 37.5 \text{ mL} = 112.5 \text{ mL}$$



Initial (mol)	0.00750	0.00375	0
Change (mol)	-0.00375	-0.00375	+0.00375
After reaction (mol)	0.00375	0	0.00375
Concentration after reaction (M)	$\frac{0.00375 \text{ mol}}{0.1125 \text{ L}} = 0.0333 \text{ M}$		$\frac{0.00375 \text{ mol}}{0.1125 \text{ L}} = 0.0333 \text{ M}$

Notice that at the half-equivalence point, [weak acid] = [conjugate base]. As a result, $[\text{H}_3\text{O}^+] = K_a$ and $\text{pH} = \text{p}K_a$.

Use the rearranged K_a expression (or the Henderson-Hasselbalch equation) to calculate pH.

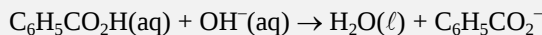
$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{C}_6\text{H}_5\text{CO}_2\text{H}]}{[\text{C}_6\text{H}_5\text{CO}_2^-]} = 6.3 \times 10^{-5} \left(\frac{0.0333}{0.0333} \right) = 6.3 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.20$$

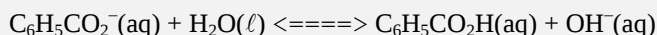
- (d) The equivalence point is reached when 75.0 mL of NaOH is added to the weak acid solution. All of the acid in the flask and the added base is consumed, forming the water and the conjugate base, $\text{C}_6\text{H}_5\text{CO}_2^-$. The solution now contains a weak base and the pH can be calculated using the methods introduced in Section 16.4.

$$\text{mol CH}_3\text{CO}_2\text{H} = \text{mol OH}^- = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol CH}_3\text{CO}_2\text{H}$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 75.0 \text{ mL} = 150.0 \text{ mL}$$



Initial (mol)	0.00750	0.00750	0
Change (mol)	-0.00750	-0.00750	+0.00750
After reaction (mol)	0	0	0.00750
Concentration after reaction (M)			$\frac{0.00750 \text{ mol}}{0.1500 \text{ L}} = 0.0500 \text{ M}$



$$K_b(\text{C}_6\text{H}_5\text{CO}_2^-) = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10}$$

$$[\text{OH}^-] = \sqrt{K_b \times [\text{C}_6\text{H}_5\text{CO}_2^-]_0} = \sqrt{(1.6 \times 10^{-10})(0.0500)} = 2.8 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(2.8 \times 10^{-6}) = 5.55$$

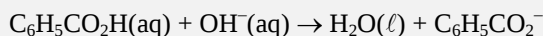
$$\text{pH} = 14.00 - \text{pOH} = 8.45$$

- (e) After the equivalence point, all of the weak acid has been consumed and the solution contains the conjugate base and excess NaOH. The benzoate ion is a much weaker base than NaOH, so the pH is controlled by the hydroxide ion concentration in solution.

$$\text{mol CH}_3\text{CO}_2\text{H} = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol CH}_3\text{CO}_2\text{H}$$

$$\text{mol OH}^- = (0.1000 \text{ L})(0.100 \text{ mol/L}) = 0.01000 \text{ mol OH}^-$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 100.0 \text{ mL} = 175.0 \text{ mL}$$



Initial (mol)	0.00750	0.01000	0
Change (mol)	-0.00750	-0.00750	+0.00750
After reaction (mol)	0	0.00250	0.00750

$$\text{Concentration after reaction (M)} \quad [\text{OH}^-] = \frac{0.00250 \text{ mol}}{0.1750 \text{ L}} = 0.0143 \text{ M}$$

$$\text{pOH} = -\log(0.0143) = 1.845$$

$$\text{pH} = 14.000 - 1.845 = 12.155$$



OWL Example Problems

17.22 Weak Acid-Strong Base Titration

Figure 17.X summarizes the four important regions of a weak acid-strong base titration plot and shows graphically the relative concentrations of weak acid, conjugate base, hydronium ion, and hydroxide ion during the titration. Notice that

- the initial pH is less than 7;
- the pH rises quickly and then levels out as a buffer solution is created;
- at the half-equivalence point, the concentration of weak acid is equal to the conjugate base concentration, and $\text{pH} = \text{p}K_a$;
- the pH at the equivalence point is greater than 7 due to the presence of a weak base in solution (the conjugate base); and
- the pH after the equivalence point is high due to the presence of excess strong base (OH^-).

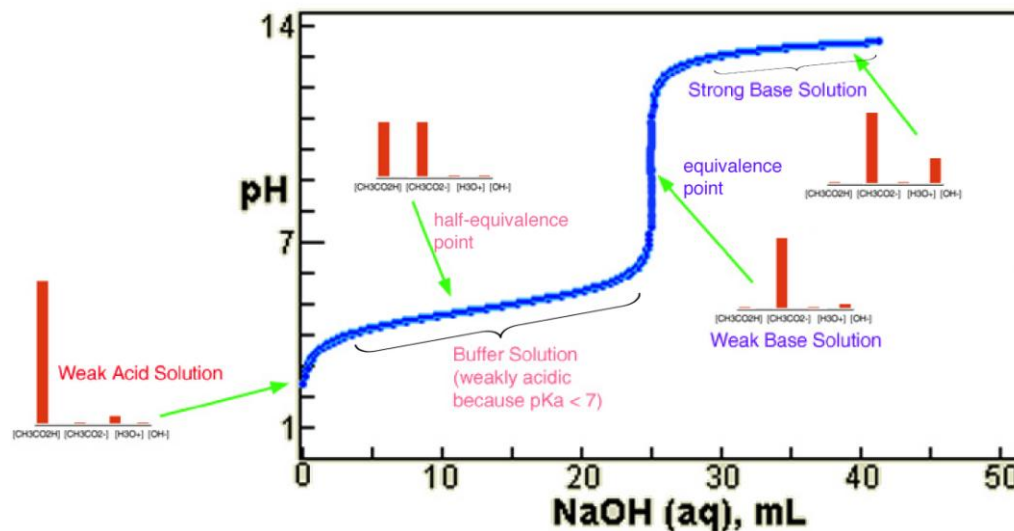


Figure 17.X Important regions of a weak acid-strong base titration plot



OWL Concept Exploration
17.21 Interpreting Titration Plots: Tutor

Note: This figure will be redone so it matches other pH plots

Weak Base-Strong Acid Titration

The shape of the titration plot for a weak base-strong acid titration (Figure 17.X) is very similar to that of a weak acid-strong base titration plot. In this case, however, the initial pH is basic and decreases as strong acid is added to the weak base.

There are four regions of interest in the pH plot for the titration of 75.0 mL of 0.100 M ammonia ($K_b = 1.8 \times 10^{-5}$) with 0.100 M HCl:

1. The initial pH is greater than 7 because the solution contains a base.
2. As the strong acid is added, the pH drops sharply and then decreases gradually until the equivalence point is reached. This is the buffer region of the titration, where the solution contains a weak acid and its conjugate base. At the midpoint of this region, half of the base originally present in the flask has been consumed and the **half-equivalence point**, also called the titration midpoint, is reached. As shown in the example problem that follows, at this point in the titration the solution pOH is equal to the weak base pK_b .
3. Near the equivalence point, where the base is completely consumed by added acid, the pH decreases rapidly. The pH at the equivalence point of the titration is less than 7 due to the presence of the ammonium ion, an acidic cation.
4. After the equivalence point the pH is low because it contains excess strong acid.

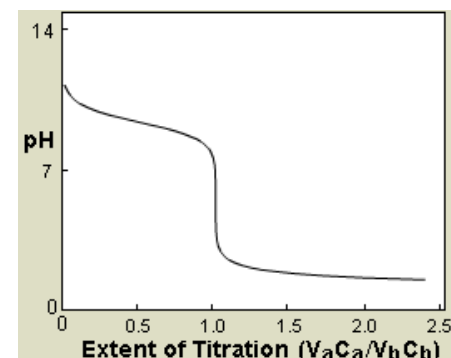


Figure 17.X Weak base-strong acid pH titration plot

The calculation of solution pH for a weak base-strong acid titration is very similar to the calculations used in the weak acid-strong base titration, as shown in the following example.

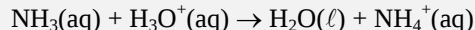
EXAMPLE PROBLEM: Weak Base-Strong Acid Titration

Determine the pH during the titration of 75.0 mL of 0.100 M ammonia ($K_b = 1.8 \times 10^{-5}$) by 0.100 M HCl at the following points.

- (a) Before the addition of any HCl
- (b) After adding 20.0 mL of HCl
- (c) At the titration midpoint
- (d) At the equivalence point
- (e) After adding 100.0 mL of HCl

SOLUTION:

Write the balanced net ionic equation for the acid-base reaction.



- (a) Calculate the pH of the solution before adding HCl. Ammonia is a weak base and the pH of the solution is calculated using methods introduced in Section 16.4

$$[\text{OH}^-] = \sqrt{K_b \times [\text{NH}_3]_0} = \sqrt{(1.8 \times 10^{-5})(0.100)} = 0.0013 \text{ M}$$

$$\text{pOH} = -\log(0.0013) = 2.87$$

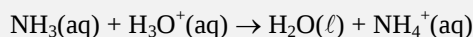
$$\text{pH} = 14.00 - \text{pOH} = 11.13$$

- (b) Before the equivalence point, all HCl is consumed by excess weak base. First consider the stoichiometry of the acid-base reaction, and then treat the solution as a buffer to calculate pH.

$$\text{mol NH}_3 = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol NH}_3$$

$$\text{mol H}_3\text{O}^+ = (0.0200 \text{ L})(0.100 \text{ mol/L}) = 0.00200 \text{ mol H}_3\text{O}^+$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 20.0 \text{ mL} = 95.0 \text{ mL}$$



<i>Initial (mol)</i>	0.00750	0.00200	0
----------------------	---------	---------	---

<i>Change (mol)</i>	-0.00200	-0.00200	+0.00200
---------------------	----------	----------	----------

<i>After reaction (mol)</i>	0.00550	0	0.00200
-----------------------------	---------	---	---------

<i>Concentration after reaction (M)</i>	$\frac{0.00550 \text{ mol}}{0.0950 \text{ L}} = 0.0579 \text{ M}$	$\frac{0.00200 \text{ mol}}{0.0950 \text{ L}} = 0.0211 \text{ M}$
---	---	---

Use the rearranged K_b expression (or the Henderson-Hasselbalch equation) to calculate pH.

$$[\text{OH}^-] = K_b \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 1.8 \times 10^{-5} \left(\frac{0.0579}{0.0211} \right) = 4.9 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(4.9 \times 10^{-5}) = 4.31$$

$$\text{pH} = 14.00 - \text{pOH} = 9.69$$

- (c) The half-equivalence point, the titration midpoint, is reached when half the amount of strong acid required to reach the equivalence point has been added to the weak base solution and, as a result, half of the weak base originally in the flask has been consumed. As shown in the weak acid-strong base titration calculations, at the midpoint in the titration $[\text{weak base}] = [\text{conjugate acid}]$. As a result, $[\text{OH}^-] = K_b$ and $\text{pOH} = \text{p}K_b$.

Example problem, continued

$$[\text{OH}^-] = K_b \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = 14.00 - \text{pOH} = 9.26$$

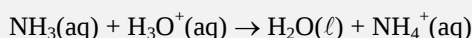
Alternately, the Henderson-Hasselbalch equation shows that at the half-equivalence point in a weak base-strong acid titration, the solution pH is equal to the conjugate acid $\text{p}K_a$ ($K_a[\text{NH}_4^+] = 5.6 \times 10^{-10}$).

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = -\log(5.6 \times 10^{-10}) + \log(1) = 9.26$$

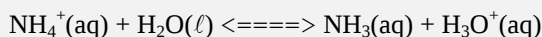
- (d) The equivalence point is reached when 75.0 mL of HCl is added to the weak acid solution. All acid and base is consumed, forming the water and the conjugate acid, NH_4^+ . The solution now contains a weak acid and the pH can be calculated using the methods introduced in Section 16.4.

$$\text{mol NH}_3 = \text{mol H}_3\text{O}^+ = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol NH}_3$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 75.0 \text{ mL} = 150.0 \text{ mL}$$



Initial (mol)	0.00750	0.00750	0
Change (mol)	-0.00750	-0.00750	+0.00750
After reaction (mol)	0	0	0.00750
Concentration after reaction (M)	$\frac{0.00750 \text{ mol}}{0.1500 \text{ L}} = 0.0500 \text{ M}$		



$$K_a(\text{NH}_4^+) = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times [\text{NH}_4^+]_0} = \sqrt{(5.6 \times 10^{-10})(0.0500)} = 5.3 \times 10^{-6} \text{ M}$$

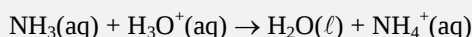
$$\text{pH} = -\log(5.3 \times 10^{-6}) = 5.28$$

- (e) After the equivalence point, all of the weak base has been consumed and the solution contains the conjugate acid and excess HCl. The ammonium ion is a much weaker acid than HCl, so the pH is controlled by the concentration of H_3O^+ in solution.

$$\text{mol NH}_3 = (0.0750 \text{ L})(0.100 \text{ mol/L}) = 0.00750 \text{ mol NH}_3$$

$$\text{mol H}_3\text{O}^+ = (0.1000 \text{ L})(0.100 \text{ mol/L}) = 0.01000 \text{ mol H}_3\text{O}^+$$

$$\text{Total volume of solution} = 75.0 \text{ mL} + 100.0 \text{ mL} = 175.0 \text{ mL}$$



Initial (mol)	0.00750	0.01000	0
Change (mol)	-0.00750	-0.00750	+0.00750
After reaction (mol)	0	0.00250	0.00750
Concentration after reaction (M)	$[\text{H}_3\text{O}^+] = \frac{0.00250 \text{ mol}}{0.1750 \text{ L}} = 0.0143 \text{ M}$		

$$\text{pH} = -\log(0.0143) = 1.845$$



OWL Example Problems
17.23 Weak Base-Strong Acid Titration

pH Titration Plots as an Indicator of Acid Strength

We have examined and explained the important features of pH titration plots in the preceding section. These titration plots (Figure 17.X) can be used to determine the

Chapter Goals Revisited

- Interpret acid-base titration plots.

Identify the type of acid-base titration, the relative strength of the acid or base being titrated, and the weak acid K_a or weak base K_b from a pH titration plot.

species being titrated, the relative strength of the acid (or base) being titrated and to determine the K_a value for the weak acid (or K_b value for the weak base) being titrated.

The initial pH is an indicator of the species being titrated. A strong or weak acid solution will have a $\text{pH} < 7$ before the addition of base, and a strong or weak base solution will have a $\text{pH} > 7$ before the addition of acid.

The relative strength of the acid or base being titrated can be determined by the pH at the equivalence point of the titration:

- If $\text{pH} = 7$ at the equivalence point, the acid (or base) being titrated is strong. At the equivalence point in a strong acid (or strong base) titration, the solution contains water and a neutral salt.
- If $\text{pH} > 7$ at the equivalence point, the acid being titrated is weak. At the equivalence point in a weak acid-strong base titration, the solution contains the conjugate base of the weak acid (as one component of a basic salt). The relative strength of the weak acid cannot be determined from a pH titration plot because it also depends on the initial acid concentration and the concentration of the titrant.
- If $\text{pH} < 7$ at the equivalence point, the base being titrated is weak. At the equivalence point in a weak base-strong acid titration, the solution contains the conjugate acid of the weak base (as one component of an acidic salt). The relative strength of the weak base cannot be determined from a pH titration plot because it also depends on the initial base concentration and the concentration of the titrant.

The K_a for a weak acid (or K_b for a weak base) can be determined from the pH at the half-equivalence point in an acid-base titration.

- In a weak acid-strong base titration, $[\text{weak acid}] = [\text{conjugate base}]$ at the half-equivalence point (titration midpoint) and $\text{pH} = \text{p}K_a$ for the weak acid.
- In a weak base-strong acid titration, the pH at the half-equivalence point (titration midpoint) is equal to the $\text{p}K_a$ of the conjugate acid. Because $K_a \cdot K_b = K_w$ for any acid-base conjugate pair, the K_b for the weak base can then be calculated.

Flashback

17.1 Acid-Base Reactions



17.X Acid-Base Reactions

Note that if the weak acid is relatively strong ($K_a > 10^{-3}$) or if the solution is very dilute ($[\text{weak acid}] < 10^{-3} \text{ M}$), the pH at the titration midpoint will vary slightly from the acid $\text{p}K_a$.

Flashback

16.3 Acid and Base Strength



16.14 The K_a - K_b relationship

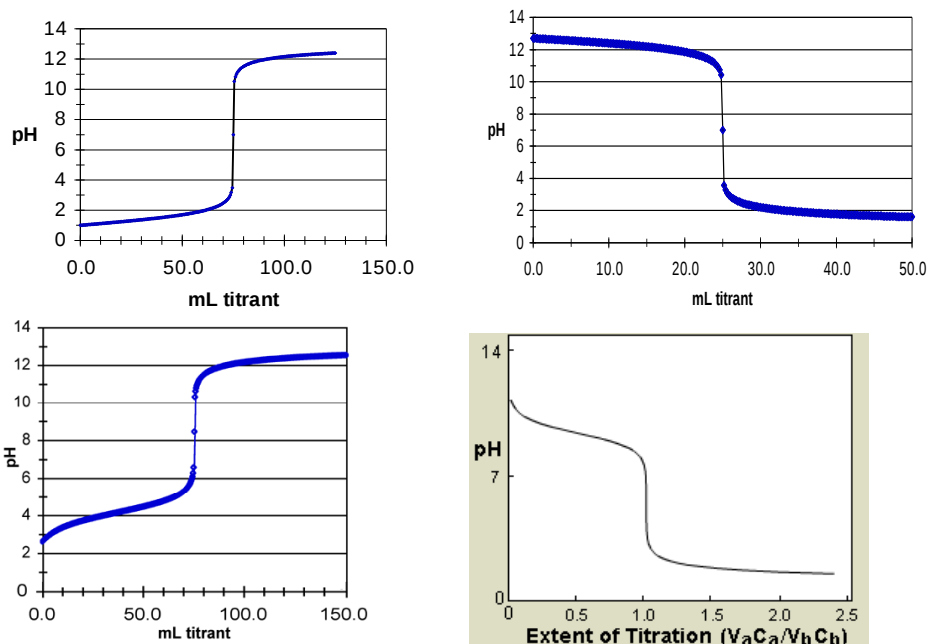


Figure 17.X pH plots for (a) strong acid-strong base, (b) strong base-strong acid, (c) weak acid-strong base, and (d) weak base-strong acid titrations

Detecting pH

The pH of an acidic or basic solution can be determined using an acid-base indicator or a pH meter. Acid-base indicators are weak organic acids that can be used to indicate the pH of a solution because the acid form of the indicator has a different color than its conjugate base, and because the color change takes place over a relatively narrow pH range. Some common acid-base indicators are shown in Figure 17.X.

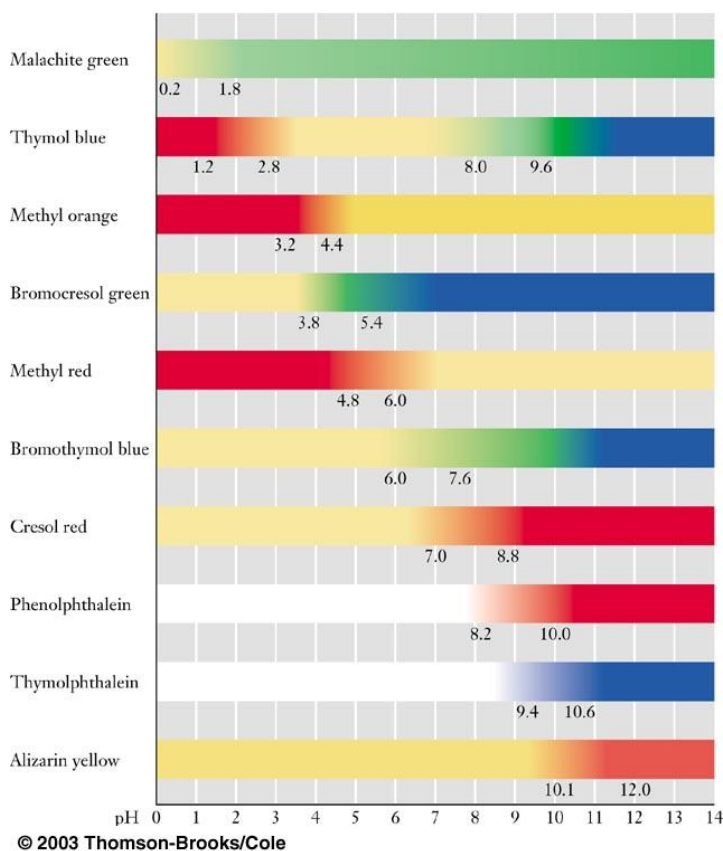


Figure 17.XX Some acid-base Indicators

Indicators are chosen for acid-base titrations based on the pH at the titration equivalence point, which is determined by the substance being titrated. The indicator color change is visible over a pH range given approximately by indicator $pK_a \pm 1$. A color change in the indicator is intended to signal that the equivalence point in the titration has been reached. To ensure that this will happen, the pK_a of the indicator should be as close as possible to the pH at the equivalence point of the titration.

In the titration of a strong acid with a strong base, the pH change is so large in the immediate vicinity of the equivalence point that a variety of indicators can be used successfully. A common indicator chosen for strong acid-strong base titrations (pH = 7.00 at the equivalence point) is phenolphthalein, but as shown in Figure 17.X, bromothymol blue or bromocresol green could also be used.

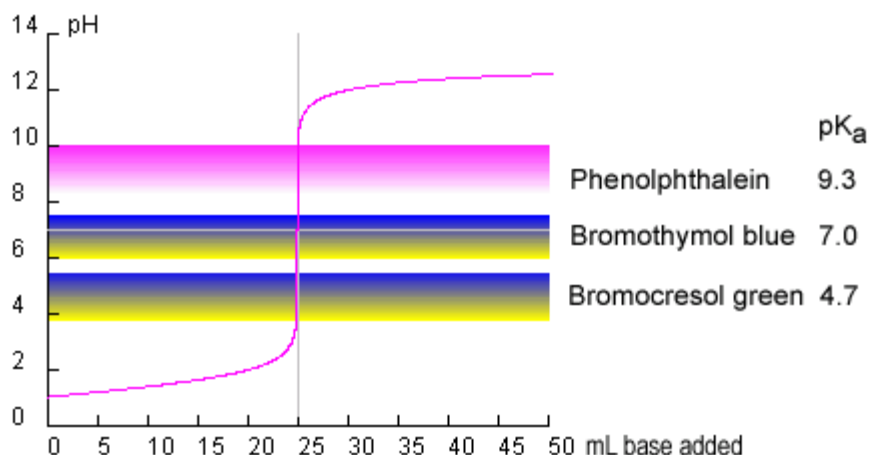


Figure 17.XX Indicator choices for a strong acid-strong base titration

When weak acids and/or bases are involved, the pH range is smaller and the choice of indicator is more critical. The benzoic acid-sodium hydroxide titration described earlier has a pH of 8.45 at the equivalence point. The indicator cresol red could be used to detect the equivalence point of this titration.

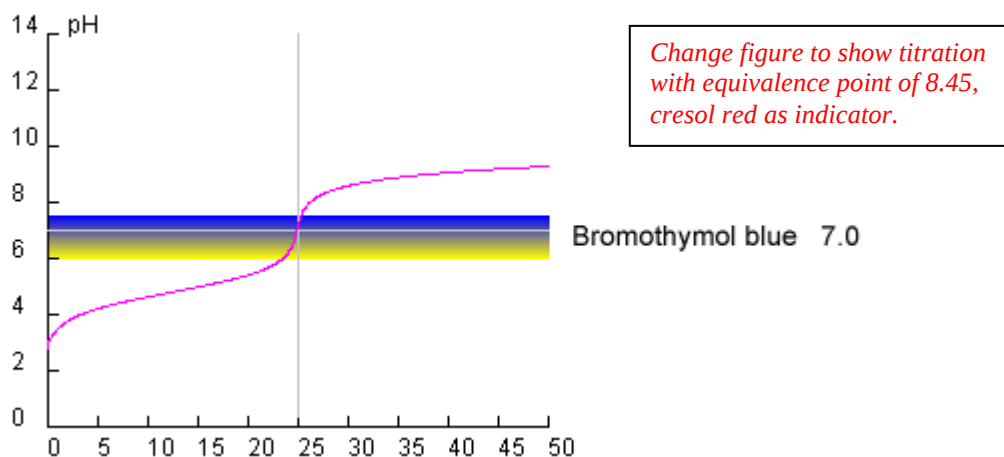


Figure 17.XX Indicator choice for a weak acid-weak base titration



OWL Concept Exploration
17.24 Acid-Base Indicators

4. Polyprotic Acids



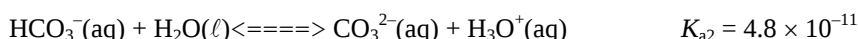
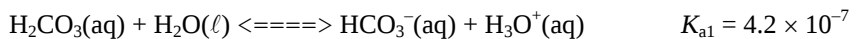
OWL Opening Exploration
17.25 ???: Simulation
17.25 Polyprotic Acid Solutions

In the previous chapter you were introduced briefly to polyprotic acids, Brønsted-Lowry acids that can donate more than one proton to a base. We now consider this class of acids in more detail by studying the concentration of all species in a solution containing a polyprotic acid and the titration of a polyprotic acid.

Flashback

16.1 Acids and Bases:
Introduction and
Definitions

Carbonic acid is an example of a diprotic acid, an acid that can donate a total of two protons to a base.



Recall from Section 17.2 that when the solution pH is equal to the weak acid $\text{p}K_a$, equal amounts of weak acid and conjugate base are found in solution. Here the diprotic acid has two K_a values and thus there are two points where pH is equal to $\text{p}K_a$ (at $\text{p}K_{a1}$ and $\text{p}K_{a2}$). This is shown in alpha plot for the carbonic acid-bicarbonate ion-carbonate ion system (Figure 17.X), in which there are two points where $\alpha = 0.5$ and $\text{pH} = \text{p}K_a$. In addition, notice that

- At pH values below $\text{p}K_{a1}$ the system contains mostly H_2CO_3 .
- At intermediate pH (between $\text{p}K_{a1}$ and $\text{p}K_{a2}$) the system contains mostly HCO_3^- .
- At high pH, above $\text{p}K_{a2}$, the system contains mostly CO_3^{2-} .

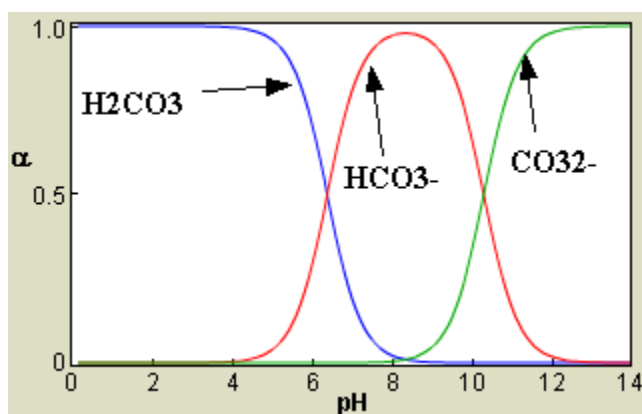


Figure 17.X Carbonic Acid Alpha Plot

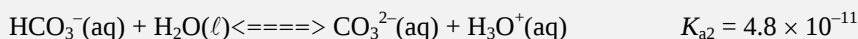
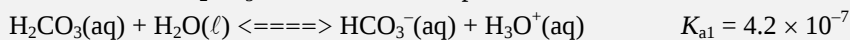
The concentrations of species in a polyprotic acid solution can be calculated using the same techniques and assumptions used when considering buffer solutions. The approach involves first identifying the species present in significant quantities in the solution, then determining the reaction that represents the predominant equilibrium in solution, and finally solving the equilibrium system using an *ICE* table.

Chapter Goals Revisited

- Apply the principles of acid-base equilibria to aqueous solutions of polyprotic acids.
Calculate the concentration of all species present in a polyprotic acid solution.

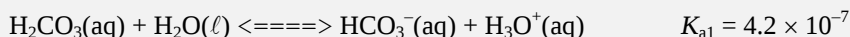
EXAMPLE PROBLEM:

For a 0.20 M solution of H_2CO_3 , calculate both the pH and the carbonate ion concentration.



SOLUTION:

Step 1. In order to calculate pH, recognize that because K_{a1} is much greater than K_{a2} the predominant species in solution are H_2CO_3 , HCO_3^- , and H_3O^+ .



Step 2. Set up an *ICE* table for the first acid hydrolysis.

	$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
Initial (M)	0.20	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.20 - x$	x	x

Example problem, continued

Step 3. Substitute these equilibrium concentrations into the K_{a1} expression and calculate the pH of the solution.

$$K_{a1} = 4.2 \times 10^{-7} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{0.20 - x} = \frac{x^2}{0.20}$$

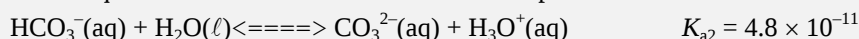
Because the value of K_{a1} is small when compared to the initial acid concentration, it is reasonable to assume that the amount of weak acid ionized (x) is very small when compared to $[\text{H}_2\text{CO}_3]_0$.

$$x = [\text{H}_3\text{O}^+] = \sqrt{K_{a1} \times 0.20} = 2.9 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(2.9 \times 10^{-4}) = 3.54$$

Notice that in the carbonic acid alpha plot above, at a pH of about 3.5 the predominant species in solution is H_2CO_3 . It is reasonable to assume that the second ionization is not important in determining the pH of this solution.

Step 4. Use the equation for the second ionization and the pH of the solution to determine the carbonate ion concentration.



Step 5. Set up an ICE table for the second acid hydrolysis.

	$\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
Initial (M)	2.9×10^{-4}	0	2.9×10^{-4}
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$2.9 \times 10^{-4} - x$	x	$2.9 \times 10^{-4} + x$

Step 3. Substitute these equilibrium concentrations into the K_{a2} expression and solve for x , the carbonate ion concentration.

$$K_{a2} = 4.8 \times 10^{-11} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = \frac{(x)(2.9 \times 10^{-4} + x)}{2.9 \times 10^{-4} - x} = \frac{x(2.9 \times 10^{-4})}{2.9 \times 10^{-4}}$$

The value of K_{a2} is very small when compared to $[\text{H}_3\text{O}^+]$ and $[\text{HCO}_3^-]$, so it is reasonable to assume that x is very small when compared to $[\text{H}_2\text{CO}_3]_0$.

$$x = [\text{CO}_3^{2-}] = K_{a2} = 4.8 \times 10^{-11} \text{ M}$$

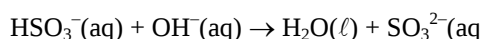
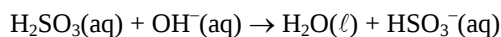
Notice that the carbonate ion concentration is equal to the K_{a2} value for this weak acid.



OWL Example Problems
17.X Polyprotic acids

Polyprotic Acid Titration Plots

The pH plot for the titration of sulfurous acid, H_2SO_3 with a strong base (Figure 17.X) shows two distinct equivalence points where the two protons are removed stepwise by reaction with OH^- .



Although the presence of two inflection points in Figure 17.X clearly indicates that this is the titration of a diprotic acid, there are cases when a polyprotic acid titration plot does not show all of the possible equivalence points.

Figure 17.X shows a series of calculated pH plots for the titration of weak diprotic acids with $\text{p}K_{a1} = 3$ and $\text{p}K_{a2}$ values between 7 and 4. Notice that when the difference between $\text{p}K_{a1}$ and $\text{p}K_{a2}$ is greater than or equal to 3, two distinct equivalence points are observed in the titration plot. However, when the two equilibrium constants are relatively similar ($\Delta\text{p}K_a < 3$), only a single equivalence point is observed. Thus it is important to remember that the presence of a single equivalence point in a titration plot does not

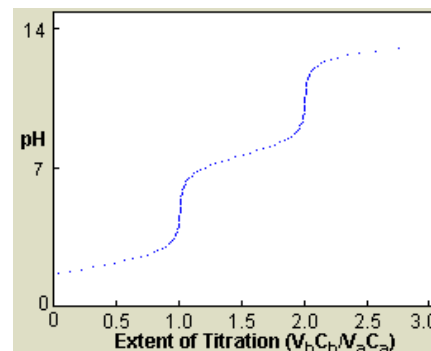


Figure 17.X pH plot for the titration of H_2SO_3 with NaOH

necessarily indicate the presence of a monoprotic acid. It could be due to the titration of a diprotic acid where K_{a1} and K_{a2} values are similar.

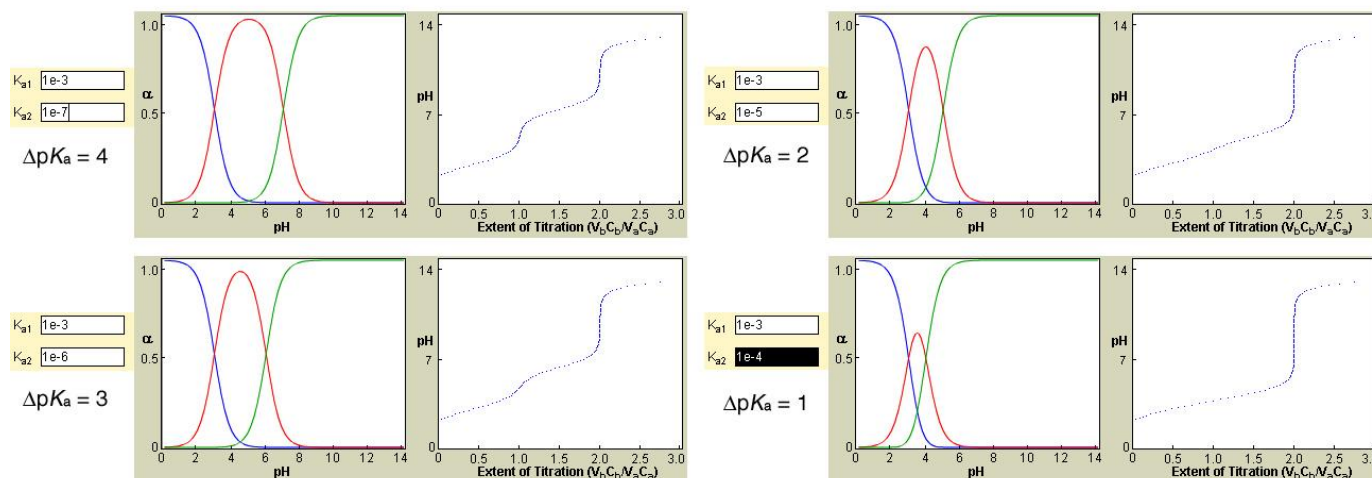


Figure 17.X Alpha plots and pH plots for a series of diprotic acids

17.5 Two Important Acid-Base Systems



OWL Opening Exploration
17.X

There are two very important acid-base systems that deserve closer examination, particularly with respect to the importance of their acid-base properties to biological functions.

The Carbonate System: $\text{H}_2\text{CO}_3/\text{HCO}_3^-/\text{CO}_3^{2-}$

The carbonic acid-bicarbonate ion-carbonate ion system is the principal buffer system in our blood. The alpha plot for this system is shown below.

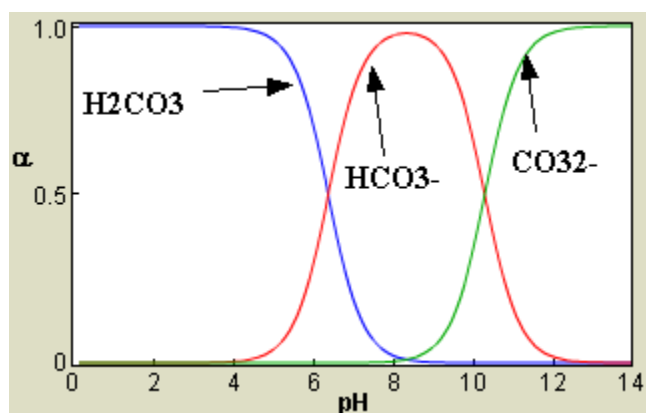
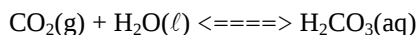


Figure 17.XX

The pH of blood is typically about 7.4. The alpha plot shows that, at this pH, the concentration of carbonate ion, CO_3^{2-} , is very low in the blood and that the concentrations of both H_2CO_3 and HCO_3^- are significant ($[\text{HCO}_3^-] \gg [\text{H}_2\text{CO}_3]$).

Blood pH is regulated in part by CO_2 respiration. In the body, carbon dioxide reacts with water to form carbonic acid.

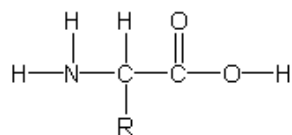


Under conditions of respiratory acidosis, an excess of acid in body fluids, exhaling large amounts of CO_2 will decrease the concentration of H_2CO_3 in the blood. This shifts the buffer position to the right on the alpha plot and pH decreases. The opposite

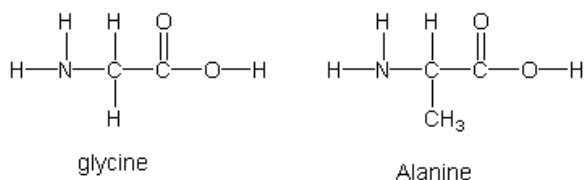
When CO_2 is lost from the body (when you exhale or hyperventilate), the concentration of H_2CO_3 in the blood decreases. This represents a shift to the right on the alpha plot, to higher pH. Excess hyperventilation can cause respiratory alkalosis, an excess of base in body fluids. Breathing into a paper bag can increase the CO_2 levels in the body, increasing $[\text{H}_2\text{CO}_3]$ and decreasing the pH of body fluids such as blood.

Amino Acids

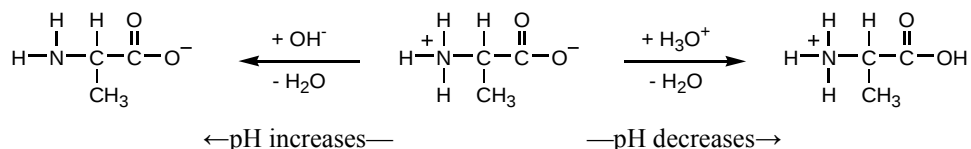
Amino acids are the building blocks of proteins in our bodies. There are a large number of amino acids known, and 21 are essential for human life. All have the basic structure shown below:



Amino acids contain both a carboxylic acid group ($-\text{CO}_2\text{H}$) and an amino group ($-\text{NH}_2$). The central, sp^3 -hybridized carbon, called the alpha carbon, is bonded to the carboxylic acid group, the amino group, a hydrogen atom, and a fourth group, labeled R. The R group is different for each different amino acid and can be pH neutral, acidic, or basic. Two of the simplest amino acids are glycine ($\text{R} = \text{H}$) and alanine ($\text{R} = \text{CH}_3$).



Although amino acids are often written as shown above, with $-\text{CO}_2\text{H}$ and $-\text{NH}_2$ groups, this is not an accurate representation. Amino acids exist as **zwitterions**, compounds containing both a positive and negative charge, when dissolved in water, in bodily fluids, and in the solid state. Increasing the pH of a solution containing an amino acid deprotonates the zwitterion, and decreasing the pH protonates the zwitterion.



The pH at which an amino acid has equal numbers of positive and negative charges is called the **isoelectric point** (pI). Each different amino acid has a unique isoelectric point. Most of the amino acids have pI values near 6, with the exception of the amino acids with acidic side groups (lower pI values) and the amino acids with basic side groups (higher pI values).

Zwitterionic amino acids can act as buffers, absorbing acid or base to produce the fully protonated or fully deprotonated form, respectively. Under physiological pH conditions,

amino acids exist almost exclusively in the zwitterionic form, as shown by the alpha plot for glycine (Figure 17.X).

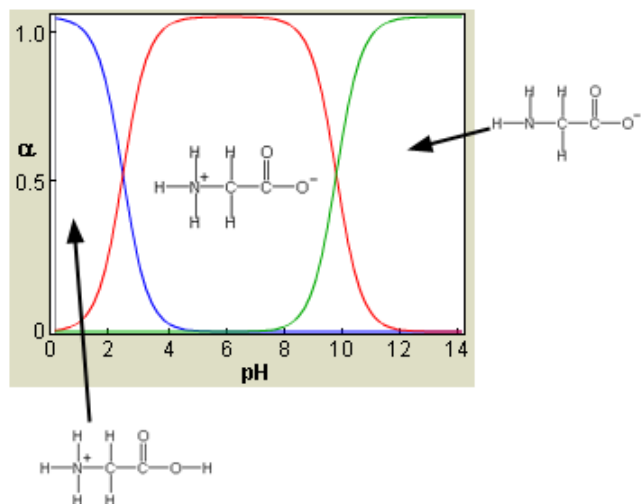


Figure 17.X



OWL Concept Exploration
17.X Amino Acids



OWL Summary Assignments
17.XX Chapter Review
17.XX Challenging Problems

Key Equations

Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} \quad (17.1)$$

Key Terms

(should this be key terms and concepts? Review of A-B titrations?)

Alpha plot

Half-equivalence point

Isoelectric point

Zwitterion