

CHAPTER 7

Mixtures of Acids and Bases

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7.0 INTRODUCTION

In Chapter 6, we examined the equilibrium concentrations in solutions of acids and solutions of bases. In this chapter, we continue our discussion of acids and bases by focusing on the equilibrium concentrations of solutions formed by mixing acids and bases.

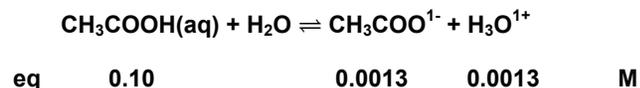
THE OBJECTIVES OF THIS CHAPTER ARE TO:

- explain the common ion effect;
- define buffers and explain their use;
- show how the composition of a mixture varies with its pH;
- describe titration curves, how they are generated, and what they mean; and
- describe acid-base indicators and explain their function.

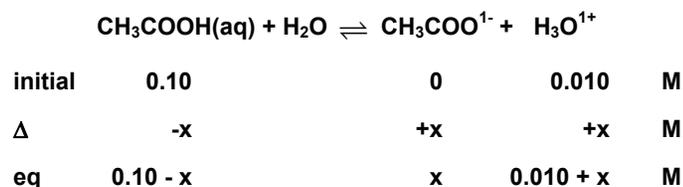
7.1 THE COMMON-ION EFFECT

When solutions are prepared in such a way that there are two or more separate sources of an ion in equilibrium, then that ion is referred to as a **common ion**. In this and the following chapters, we will have occasion to deal with the effect on an equilibrium mixture caused by the addition of a common ion. The effect can readily be predicted with Le Châtelier's principle, which predicts that the composition of the mixture shifts to counteract the addition. Consequently, *the addition of a common ion always produces more of the substances on the opposite side of the equilibrium and reduces the concentrations of the other substances on the same side of the equilibrium.*

In Example 6.7, we determined that the equilibrium concentrations in a 0.10 M solution of acetic acid are the following:



When hydrochloric acid is added to acetic acid, the H_3O^{1+} ion is common to both solutions, so it is a common ion. The additional hydronium ion from the hydrochloric acid reacts with the acetate ion above to increase the concentration of acetic acid and decrease the concentration of acetate ion. Thus, less acetic acid reacts with water to produce acetate ion in the presence of the common ion, or, said slightly differently, *addition of hydronium ion suppresses (reduces the extent of) the dissociation of the weak acid* as a result of the common-ion effect. For example, consider the following reaction table for the dissociation of 0.10 M acetic acid in the presence of 0.010 M hydronium ion:



$$K_a = \frac{[\text{CH}_3\text{COO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{CH}_3\text{COOH}]} = \frac{x(0.010 + x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

The common ion suppresses the dissociation, so $x < 0.0013$ M - its value in the absence of excess hydronium ion. If x is negligible compared to 0.01 then the equilibrium concentrations of acetic acid and hydronium ion are $[\text{CH}_3\text{COOH}] = 0.10 - x = 0.10$ M and $[\text{H}_3\text{O}^{1+}] = 0.01 + x = 0.01$ M. Solving the K_a expression for x , we obtain the following:

$$x = [\text{CH}_3\text{COO}^{1-}] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^{1+}]} = (1.8 \times 10^{-5}) \left(\frac{0.10}{0.010} \right) = 1.8 \times 10^{-4} \text{ M}$$

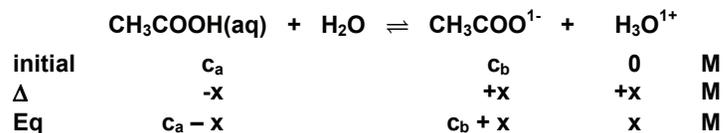
The hydronium ion concentration in the final solution is $0.010 + 0.00018 = 0.010$ M as x is negligible. We conclude that, *in a solution containing both a weak acid and a strong acid, the hydronium ion produced by the weak acid can usually be ignored because of the common-ion effect*. The same conclusion can be drawn for a solution containing both a strong base and a weak base. *The amount of hydroxide ion produced by a weak base in the presence of a strong base is usually negligible in determining the hydroxide ion concentration*.

7.2 BUFFERS

In Chapter 6, we treated in some detail four types of acid-base solutions: strong acid, strong base, weak acid, and weak base. We now treat buffers, the last type of acid-base solution to be considered. A buffer is defined in the dictionary as a “device that softens the shock of a blow.” A chemical buffer serves much the same purpose: it softens the effect of the shock caused by the addition of a strong acid or base. A **buffer** is a solution of a weak acid and its conjugate base in *comparable* and *appreciable* amounts. Buffers are very common both in and outside the chemistry laboratory. For example, aspirin is an acid that can upset the stomach, but Bufferin[®] contains buffers to reduce the pH changes that ordinarily accompany the addition of an acid. Much of the maintenance involved in the upkeep of an aquarium involves maintaining proper buffer levels in the water to assure that the pH stays in a range that is safe for the fish. Blood is also buffered, which is why it maintains a pH of about 7.4 even though many acid-base reactions take place in it.

Buffers are able to minimize changes in pH because they contain both a weak acid and a weak base. Thus, if a strong acid is added to a buffered solution, it reacts with the weak base component of the buffer, and if a strong base is added to a buffered solution, it reacts with the weak acid component of the buffer. Either way, the effect of the addition of hydroxide or hydronium ion on the solution is dramatically reduced because these strong acids and bases are converted into much weaker acids and bases by the action of the buffer.

Buffers contain both a weak acid and a weak base, so both K_a and K_b must be satisfied, and either can be used to determine the composition of the equilibrium mixture. However, pH is more common than pOH, so we use the acid dissociation reaction to discuss buffered solutions. Consider an acetic acid/acetate ion buffer in which the initial concentrations of the acid (c_a) and its conjugate base (c_b) are comparable. The reaction table for the acid dissociation of acetic acid in the presence of acetate ion has the following form:



The acetate ion suppresses the acid dissociation due to the common-ion effect, so x is very small. Thus, $c_a - x \sim c_a$ and $c_b + x \sim c_b$. The equilibrium constant expression is

$$K_a = \frac{[\text{CH}_3\text{COO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{CH}_3\text{COOH}]} = \frac{(c_b + x)x}{(c_a - x)} = \frac{c_b}{c_a} x = \frac{n_b}{n_a} x$$

n_b and n_a are the numbers of moles of base and acid, respectively. The ratio of concentrations is equal to the ratio of moles because the volumes cancel in the ratio:

$$\frac{c_b}{c_a} = \frac{n_b/V}{n_a/V} = \frac{n_b}{n_a}$$

Solving for x yields the hydronium ion concentration.

$$[\text{H}_3\text{O}^{1+}] = x = K_a \times \frac{c_a}{c_b} = K_a \times \frac{n_a}{n_b} \quad \text{Eq. 7.1}$$

Taking the negative logarithm of both sides of Equation 7.1, we obtain the pH of a buffer solution as a function of the $\text{p}K_a$ of the acid and the ratio of the numbers of moles or concentrations of the base and the acid.

$$\text{pH} = \text{p}K_a + \log\left(\frac{c_b}{c_a}\right) = \text{p}K_a + \log\left(\frac{n_b}{n_a}\right) \quad \text{Eq. 7.2}$$

Equation 7.2 is known as the **Henderson-Hasselbalch equation**.

Example 7.1

What is the pH of a solution that is 0.600 M potassium acetate and 0.750 M acetic acid?

This is a solution of a weak acid (acetic acid) and its conjugate base (acetate ion) in comparable and appreciable amounts. Consequently, it is a buffered solution, and Equation 7.2 can be used to determine the pH. The $\text{p}K_a$ of acetic acid is obtained from Appendix C to be 4.74. Substitution into Equation 7.2 yields

$$\text{pH} = \text{p}K_a + \log\left(\frac{c_b}{c_a}\right) = 4.74 + \log\left(\frac{0.600}{0.750}\right) = 4.64$$

BUFFER ACTION

Buffers act to protect the solution from drastic pH changes resulting from the addition of hydronium or hydroxide ions by converting the added ions into a weak acid or weak base. Unreacted hydronium or hydroxide ions produce large changes in pH, so the buffer must be in excess to function properly, which is why it must be present in appreciable amounts. When a strong acid is added to a buffer, it reacts with the weak base, but when a strong base is added, it reacts with the weak acid. *Acid-base reactions involving OH^{1-} or H_3O^{1+}*

PRACTICE EXAMPLE 7.1

What is the pH of a buffer prepared by dissolving 23.5 g of KNO_2 ($M_m = 85.1 \text{ g}\cdot\text{mol}^{-1}$) in 1.25 L of 0.0882 M HNO_2 ?

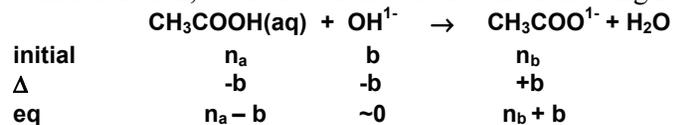
$\text{p}K_a$ of $\text{HNO}_2 =$ _____ from Appendix C

moles of KNO_2 in solution :

moles of HNO_2 in solution = _____ mol

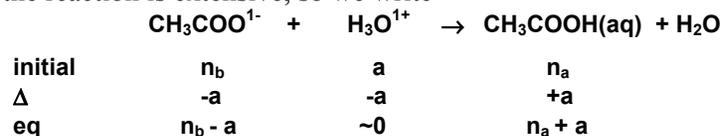
pH = _____ mol

ions are always extensive, so essentially all of the limiting reactant disappears, i.e., the delta line is known. Consider the case where b moles of OH^{1-} ion are added to a buffer solution that contains n_a moles of acetic acid and n_b moles of acetate ion. The strong base reacts extensively with the weak acid in the buffer. Acetic acid must be in excess ($n_a > b$) to have proper buffer function, so the reaction table has the following form:



The reaction replaces the OH^{1-} ion, a strong base, with $\text{CH}_3\text{COO}^{1-}$ ions, a weak base, which causes the pH change caused by the addition of the strong base to be considerably less than it would have been in the absence of the buffer.

If hydronium ion is added to the buffer solution, the weak base, which must be in excess, goes to work. The reaction table for the addition of a moles of acid to a buffer solution containing n_b moles of weak base and n_a moles of weak acid has the following form. Again, the reaction is extensive, so we write



The effect is to replace the strong acid with a weak acid, which minimizes the drop in pH.

Example 7.2

By how much would the pH of 200. mL of water change when 10. mL of 6.0 M NaOH is added to it?

We assume pure water at 25 °C, so the initial pH is 7.00. We determine the hydroxide ion concentration (the final solution contains 60. mmol of OH^{1-} in 210 mL of solution), convert that to a pOH, and the pOH into the pH.

$$[\text{OH}^{1-}] = \frac{60 \text{ mmol}}{210 \text{ mL}} = 0.29 \text{ M}$$

$$\text{pOH} = -\log(0.29) = 0.54; \text{ pH} = 14.00 - 0.54 = 13.46$$

The final pH is 13.46 and the initial pH was 7.00, so the pH change is

$$\Delta\text{pH} = \text{pH}_{\text{final}} - \text{pH}_{\text{initial}} = 13.46 - 7.00 = 6.46$$

Example 7.3

By how much would the pH of 200. mL of the buffer described in Example 7.1 change when 10. mL of 6.0 M NaOH is added?

Dilution effects of mixing two solutions can be avoided by doing the problem in moles. Thus, we first determine the initial number of moles (or millimoles since the volumes are in mL) of the relevant species.

$$(200. \text{ mL})(0.750 \text{ mmol CH}_3\text{COOH/mL}) = 150. \text{ mmol CH}_3\text{COOH}$$

$$(200. \text{ mL})(0.600 \text{ mmol CH}_3\text{COO}^-/\text{mL}) = 120. \text{ mmol CH}_3\text{COO}^-$$

$$(10. \text{ mL})(6.0 \text{ mmol OH}^-/\text{mL}) = 60. \text{ mmol OH}^-$$

The reaction table for this extensive reaction is

	$\text{CH}_3\text{COOH(aq)} + \text{OH}^-$		\rightleftharpoons	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O}$	
initial	150	60		120	mmol
Δ	-60	-60		+60	mmol
final	90	~ 0		180	mmol

The final mixture still contains appreciable and comparable amounts of the acid and its conjugate base, so it can still be treated as a buffer solution.

$$\text{pH} = \text{pK}_a + \log\left(\frac{n_b}{n_a}\right) = 4.74 + \log\left(\frac{180}{90}\right) = 5.04$$

The addition of the base caused the pH of the solution to rise from an original pH of 4.64 (Example 7.1) to a final pH of 5.04.

$$\Delta\text{pH} = \text{pH}_{\text{final}} - \text{pH}_{\text{initial}} = 5.04 - 4.64 = 0.40$$

The function of a buffer can be seen clearly by comparing the results of Examples 7.2 and 7.3. Adding 60 mmol OH^- to 200 mL of water resulted in $\Delta\text{pH} = 6.46$, which implies a change in hydronium ion concentration by a factor of $10^{6.46}$, which is 2.9×10^6 or about three million. Adding the same 60 mmol of hydroxide to 200 mL of the buffer increased the pH by only 0.40 pH units, which is change in hydronium ion concentration by a factor of $10^{0.40} = 2.5$. Thus, adding 60 mmoles of hydroxide to this buffer decreases hydronium ion three-fold, while adding it to water decreases it by three million-fold! The effect of a strong acid on a buffer solution is examined in Example 7.4.

When a strong acid is added to a buffer, the resulting solution will be a buffer as long as the hydronium ion is the limiting reactant, but if the hydronium ion is in excess, then the resulting solution is a strong acid solution, and the pH is determined from the concentration of the excess hydronium ion. Similar considerations apply to the addition of a strong base to a buffer: if the hydroxide ion is in excess, the resulting solution is a strong base and the pH is determined from the concentration of the excess hydroxide ion.

Example 7.4

By how much would the pH of 200. mL of the buffer described in Example 7.1 change when 10. mL of 6.0 M HCl is added?

The initial number of mmoles of hydronium is (10. mL)(6.0 mmol H₃O¹⁺/mL) = 60. mmol H₃O¹⁺. (See Example 7.3 for the determination of the initial numbers of millimoles of acetic acid and acetate ion.) The reaction table for the extensive reaction between the added acid and the base component of the buffer is

	$\text{H}_3\text{O}^{1+} + \text{CH}_3\text{COO}^{1-} \rightarrow \text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}$			
initial	60	120	150	mmol
Δ	-60	-60	+60	mmol
Final	~0	60	210	mmol

The resulting solution is still a buffer because it still has appreciable and comparable amounts of the weak acid and its conjugate base. Thus, Equation 7.2 can be used to obtain the pH.

$$\text{pH} = \text{pK}_a + \log\left(\frac{n_b}{n_a}\right) = 4.74 + \log\left(\frac{60.}{210.}\right) = 4.20$$

The initial pH was 4.64 (Example 7.1), so the addition of the strong acid results in a decrease of 0.44 pH units.

Example 7.5

What is the pH of a solution prepared by adding 30.0 mL of 12.0 M HCl to 576 mL of a buffer solution that is 0.600 M in HClO and 0.500 M in KClO?

The strong acid reacts with ClO¹⁻. The number of millimoles of each substance is determined by multiplying its volume by its molarity. The reaction table is

	$\text{H}_3\text{O}^{1+} + \text{ClO}^{1-} \rightarrow \text{HClO}(\text{aq}) + \text{H}_2\text{O}$			
Initial	360	288	346	mmol
Δ	-288	-288	+288	mmol
final	72	~0	634	mmol

There is insufficient buffer capacity, so the resulting solution is a strong acid.*

$$[\text{H}_3\text{O}^{1+}] = \frac{72 \text{ mmol}}{606 \text{ mL}} = 0.12 \text{ M}; \text{pH} = -\log(0.12) = 0.92$$

The pK_a of HClO is 7.46, so the pH of the initial buffer is $\text{pH} = 7.46 + \log\left(\frac{0.500}{0.600}\right) = 7.38$

Thus, addition of the acid lowered the pH by 6.46 units, which is over a million-fold increase in [H₃O¹⁺]. The large increase is due to an insufficient buffer capacity.

PRACTICE EXAMPLE 7.2

A buffer is 0.18 M in NO₂¹⁻ and 0.22 M in HNO₂.

a) What is the pH of the buffer?

pH = _____

b) What is the pH of a solution prepared by mixing 5.0 mL of 6.0 M NaOH with 250. mL of the buffer?

Reaction Table

in
 Δ
Eq

Type of solution at equilibrium: _____

pH = _____

c) What is the pH of a solution prepared by mixing 15.0 mL of 1.0 M HCl with 150. mL of the buffer?

Reaction Table

in
 Δ
Eq

Type of solution at equilibrium: _____

pH = _____

* Recall that the weak acid can be ignored in the presence of the strong acid due to the common ion effect.

PREPARING BUFFER SOLUTIONS

There must be appreciable amounts of the acid and its conjugate base in a buffer to assure that it has acceptable **buffer capacity**, the amount of hydronium or hydroxide ion that can be buffered without destroying the buffer's effectiveness. The buffer capacity of the buffer in Example 7.5 was exceeded because there was insufficient weak base in the buffer to handle the added acid, so the additional acid resulted in a large change in pH. A buffer solution has a large buffer capacity if it contains a large number of moles of weak acid and conjugate base; *i.e.*, if the weak acid and weak base are present in appreciable amounts.

A buffer functions best when the addition of large amounts of acid or base result in only small pH changes. The pH range over which the buffer is effective is called the **buffer range**. Figure 7.1 shows the relationship between pH and the mole fractions of the acid and the base in an acetic acid/acetate ion buffer. The buffer range is the pH range over which the mole fractions change most dramatically with pH. This assures that the pH change is small even when there is substantial reaction (large changes in mole fractions). This region is highlighted by the yellow box in Figure 7.1. The center of the buffer range is where the two mole fractions (or concentrations) are equal ($c_A/c_B = 1$). Application of Equation 7.2 to the midpoint of the buffer range along with the fact that $\log 1 = 0$ yields

$$\text{pH} = \text{pK}_a + \log 1 = \text{pK}_a$$

As shown in Figure 7.1, buffers operate acceptably in the range where the mole fractions of the acid and base lie between ~ 0.1 and ~ 0.9 , so the effective buffer range is usually assumed to be $0.1 < c_a/c_b < 10$. $\log(10) = -\log(0.10) = 1$, so we conclude that *buffers are effective within one pH unit of their pK_a, i.e.*,

$$(\text{pK}_a - 1) \leq \text{effective pH range for a buffer} \leq (\text{pK}_a + 1)$$

Example 7.6

Select a good buffer system from Appendix C for each of the following pH's.

pH = 4.50

The pK_a of the weak acid should fall between 3.5 and 5.5. There are 8 acids in Appendix C with pK_a 's in this range. Two choices include $\text{HC}_2\text{H}_3\text{O}_2/\text{C}_2\text{H}_3\text{O}_2^{1-}$ ($\text{pK}_a = 4.74$) and $\text{HCHO}_2/\text{CHO}_2^{1-}$ ($\text{pK}_a = 3.74$)

pH = 8.50

There are four weak acids in Appendix C with pK_a 's between 7.5 and 9.5. Some examples are $\text{HBrO}/\text{BrO}^{1-}$ ($\text{pK}_a = 8.70$), $\text{NH}_4^{1+}/\text{NH}_3$ ($\text{pK}_a = 9.25$) and $\text{H}_3\text{BO}_3/\text{H}_2\text{BO}_3^{1-}$ ($\text{pK}_a = 9.27$)

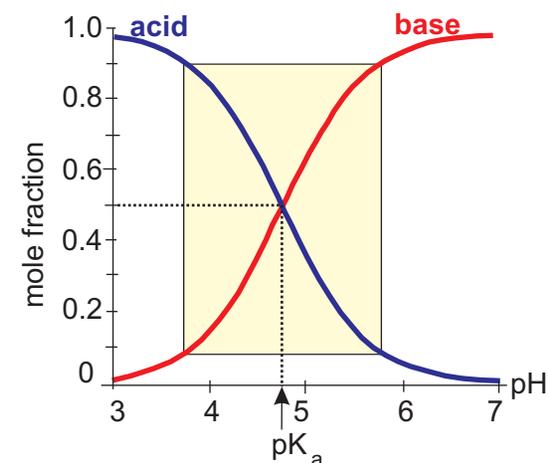


Figure 7.1 Mole fractions of acetic acid and acetate ion as a function of pH

The effective buffer range is indicated by the yellow box.

Once the conjugate acid-base pair has been selected, the ratio of their concentrations or moles that produces the desired pH must be determined by Equation 7.1, Equation 7.2, or Equation 7.3, which is obtained by rearranging either of those equations.

$$\frac{n_b}{n_a} = \frac{c_b}{c_a} = K_a \times 10^{\text{pH}} \quad \text{Eq. 7.3}$$

The ratio of the number of moles (or molarities) of base to acid required to produce a given pH equals the K_a of the acid times ten raised to the desired pH. Direct mixing of a conjugate acid and base in the ratio specified in Equation 7.3 is demonstrated in Example 7.7. It is the first of three methods to be demonstrated in this chapter.

Example 7.7

How many grams of K_2HPO_4 ($M_m = 174.17 \text{ g}\cdot\text{mol}^{-1}$) must be added to 1.00 L of 0.860 M $\text{H}_2\text{PO}_4^{1-}$ to prepare a pH = 7.00 buffer?

Equations 7.1, 7.2 or 7.3 can be used to do the problem. We will use Equation 7.3 here to demonstrate its utility. The $\text{H}_2\text{PO}_4^{1-}$ ion is the acid in this phosphate buffer, while HPO_4^{2-} is the base, so we get the K_a and $\text{p}K_a$ of $\text{H}_2\text{PO}_4^{1-}$ from Appendix C. $K_a = 6.2 \times 10^{-8}$ and $\text{p}K_a = 7.21$, and pH is given as 7.00. Substitution into Equation 7.3 yields

$$\frac{n_b}{n_a} = 6.2 \times 10^{-8} \times 10^{7.00} = \frac{0.62 \text{ mol HPO}_4^{2-}}{1 \text{ mol H}_2\text{PO}_4^{1-}}$$

Alternatively, n_b/n_a can be found with Equation 7.2 and the $\text{p}K_a$ as follows:

$$\log \frac{n_b}{n_a} = \text{pH} - \text{p}K_a = 7.00 - 7.21 = -0.21; \quad \frac{n_b}{n_a} = 10^{-0.21} = \frac{0.62 \text{ mol HPO}_4^{2-}}{1 \text{ mol H}_2\text{PO}_4^{1-}}$$

Next, determine n_a with the given volume and acid concentration.

$$n_a = 1.00 \text{ L sol'n} \times \frac{0.860 \text{ mol H}_2\text{PO}_4^{1-}}{1 \text{ L sol'n}} = 0.860 \text{ mol H}_2\text{PO}_4^{1-}$$

The given number of moles of acid is converted to mass of K_2HPO_4 with the ratio of base to acid, the number of moles of HPO_4^{1-} ion in a mole of K_2HPO_4 , and the molar mass of the base, K_2HPO_4 .

$$0.860 \text{ mol H}_2\text{PO}_4^{1-} \times \frac{0.62 \text{ mol HPO}_4^{2-}}{1 \text{ mol H}_2\text{PO}_4^{1-}} \times \frac{1 \text{ mol K}_2\text{HPO}_4}{1 \text{ mol HPO}_4^{2-}} \times \frac{174.17 \text{ g K}_2\text{HPO}_4}{1 \text{ mol K}_2\text{HPO}_4} = 93 \text{ g K}_2\text{HPO}_4$$

PRACTICE EXAMPLE 7.3

Select a conjugate acid-base pair from Appendix H to use to prepare a solution buffered to pH = 9.80.

buffer acid: _____ buffer base: _____

How many moles of the base would have to be added to 500. mL of a 0.222-M solution of the acid to prepare the buffer?

$\text{p}K_a =$ _____ from Appendix C

Use Equation 7.2 to calculate the ratio of number of moles of base to acid.

$$\log \left(\frac{n_b}{n_a} \right) =$$

$$\frac{n_b}{n_a} =$$

from the problem, $n_a =$ _____ = _____ mol

$n_b =$ _____ = _____ mol

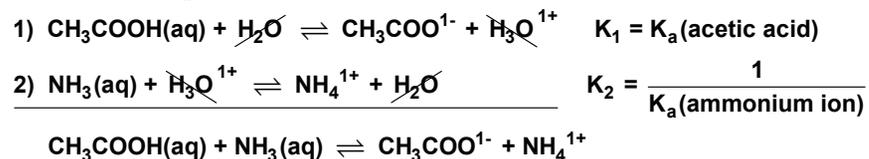
7.3 ACID-BASE COMPOSITION FROM REACTANT AMOUNTS

There are four types of acid-base reactions:

1. weak acid - weak base
2. strong acid - strong base
3. weak acid - strong base
4. strong acid - weak base

WEAK ACID - WEAK BASE REACTIONS

Reactions types 2-4 involve a strong acid and/or a strong base, so they are all extensive. However, the equilibrium constant for a weak acid and a weak base can vary from very large to very small, so it must be determined before the equilibrium composition can be determined. The equilibrium constants for weak acid-weak base reactions can be determined from the K_a 's of the reacting and produced acids because any weak acid-weak base reaction can be expressed as the sum of the acid dissociation reaction of the reacting acid and the reverse of the acid dissociation reaction of the produced acid. For example, summing the chemical equations for the acid dissociation of CH_3COOH (the reacting acid) and the reverse of the dissociation equation for NH_4^{1+} (the produced acid) produces the overall chemical equation for the reaction of acetic acid and ammonia:



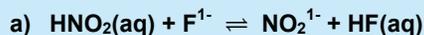
Reaction 2 is the reverse of the acid dissociation reaction of the produced acid (ammonium ion), so its equilibrium constant is the reciprocal of the K_a of the produced acid. In the addition of the two reactions, the H_2O molecules and H_3O^{1+} ions on each side of the reaction cancel to produce the desired acid-base reaction. The reaction is expressed as the sum of two reactions, so its equilibrium constant is equal to the product of the two equilibrium constants. We conclude that *the equilibrium constant of any acid-base reaction is the ratio of the reacting acid K_a to the produced acid K_a .*

$$K = K_1 \times K_2 = \frac{K_a(\text{reacting acid})}{K_a(\text{produced acid})} \quad \text{Eq. 7.4}$$

Equilibrium constants for weak acid-weak base reactions vary from very large when the reacting acid is much stronger than the produced acid to very small when the produced acid is the stronger acid. The composition of the equilibrium mixture varies accordingly.

Example 7.8

Indicate the equilibrium constant for each of the following reactions:

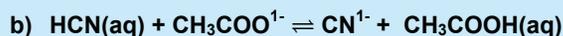


First, identify the reacting and produced acids, then obtain their K_a values from Appendix C, then use Equation 7.4 to obtain the equilibrium constant.

Reacting Acid: HNO_2 , $K_a = 4.0 \times 10^{-4}$ Produced Acid: HF , $K_a = 7.2 \times 10^{-4}$

$$K = \frac{K_a(\text{HNO}_2)}{K_a(\text{HF})} = \frac{4.0 \times 10^{-4}}{7.2 \times 10^{-4}} = 0.56$$

If the two acids have similar acid strengths, then $K \sim 1$.



Reacting Acid: HCN , $K_a = 4.0 \times 10^{-10}$ Produced Acid: CH_3COOH , $K_a = 1.8 \times 10^{-5}$

$$K = \frac{K_a(\text{HCN})}{K_a(\text{CH}_3\text{COOH})} = \frac{4.0 \times 10^{-10}}{1.8 \times 10^{-5}} = 2.2 \times 10^{-5}$$

If the reacting acid is much weaker than the produced acid, then $K \ll 1$.



Reacting Acid: HSO_4^{1-} , $K_a = 1.2 \times 10^{-2}$ Produced Acid: NH_4^{1+} , $K_a = 5.6 \times 10^{-10}$

$$K = \frac{K_a(\text{HSO}_4^{1-})}{K_a(\text{NH}_4^{1+})} = \frac{1.2 \times 10^{-2}}{5.6 \times 10^{-10}} = 2.1 \times 10^{+7}$$

If the reacting acid is much stronger than the produced acid, then $K \gg 1$.

Example 7.9

What are the equilibrium concentrations in a solution prepared by mixing 50.0 mL each of 0.10 M HBrO and 0.10 M NH_3 ?

The chemical equation: $\text{HBrO}(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{BrO}^{1-} + \text{NH}_4^{1+}$

The equilibrium constant for the reaction: $K = \frac{K_a(\text{HBrO})}{K_a(\text{NH}_4^{1+})} = \frac{2.0 \times 10^{-9}}{5.6 \times 10^{-10}} = 3.57^*$

K is not large, so the extent of reaction is unknown. Mixing the two solutions doubles their volumes, which dilutes each by a half. The reaction table therefore has the following form.

PRACTICE EXAMPLE 7.4

What is the NO_2^{1-} ion concentration in a solution prepared by mixing 75 mL of 0.10 M HNO_2 and 75 mL of 0.10 M KF ?

Initial concentrations after dilution of mixing:

$$[\text{HNO}_2] = [\text{F}^{1-}] = \text{_____ M}$$

Let x = change in concentration of $[\text{NO}_2^{1-}]$ and construct the reaction table:

rxn:

in

Δ

eq

value of $K = \text{_____}$ (From Example 7.8)

Equilibrium constant expression in terms of x :

$$K = \text{_____} = \text{_____}$$

Take square root of both sides.

Solve for x .

$$x = [\text{NO}_2^{1-}] = \text{_____}$$

* An extra significant figure has been included to avoid rounding errors.

	$\text{HBrO}(\text{aq})$	+	$\text{NH}_3(\text{aq})$	\rightleftharpoons	BrO^{1-}	+	NH_4^{1+}	
in	0.050		0.050		0		0	M
Δ	-x		-x		+x		+x	M
eq	0.050-x		0.050-x		x		x	M

The equilibrium constant expression: $K = 3.57 = \frac{x^2}{(0.050-x)^2}$

Taking the square-root of both sides: $K = \sqrt{3.57} = 1.89 = \frac{x}{(0.050-x)}$

$$x = \frac{0.0945}{2.89} = 0.033 \text{ M} = [\text{BrO}^{1-}] = [\text{NH}_4^{1+}]; [\text{HBrO}] = 0.050 - 0.033 = 0.017 \text{ M}$$

Check: $\frac{(0.0327)^2}{(0.0173)^2} = 3.57$ * ✓ The calculated concentrations reproduce K, so the algebra is correct. Note that extra significant figures are used in all concentrations.

* Extra significant digits are included in the concentrations to avoid rounding errors. Using the concentrations to two significant digits results in $K = 3.8$.

The three remaining types of acid-base reactions all involve a strong acid and/or a strong base, so they are representative of the reactions in most acid-base titrations.† Titrations are most commonly used to find the equivalence point of the reaction. However, a **titration curve**, which is a plot of solution pH versus the volume of titrant added, is an excellent way to monitor the composition of the solution, so our discussions of the remaining acid-base reactions will also include a titration curve for each type.

† Titrations were introduced in Section 2.4.

Reactions containing a strong acid and/or strong base are all characterized by large equilibrium constants, so, unlike the reaction in Example 7.9, the limiting reactant essentially disappears completely and there are no unknowns in the reaction table. The following abbreviations are used in order to discuss the various mixing problems in the most general way:

n_a = number of moles of acid added

n_b = number of moles of base added

STRONG ACID - STRONG BASE REACTIONS

Strong acids react as H_3O^{1+} in water and strong bases react as OH^{1-} , so the reaction table for the reaction n_a mol of acid and n_b mol of base if the base is the limiting reactant is

	H_3O^{1+}	+	OH^{1-}	\rightarrow	$2\text{H}_2\text{O}$
initial	n_a		n_b		
Δ	- n_b		- n_b		
eq	$n_a - n_b$		~0		

The resulting solution is a strong acid containing $(n_a - n_b)$ moles of hydronium ion. If the acid is the limiting reactant, then each entry on the Δ line would be $-n_a$ and the resulting solution would be a strong base containing $(n_b - n_a)$ moles of hydroxide ion. If $n_a = n_b$ (the equivalence point), both hydronium and hydroxide ions disappear and the resulting solution is pure water with a pH of 7. These three possibilities are summarized in Table 7.1 and demonstrated in Example 7.10.

Example 7.10

Determine the pH at each of the following points in the titration curve for the titration of 20.0 mL of 0.100 M HCl with 0.100 M NaOH that is shown in Figure 7.2.

The number of moles of acid is constant, so we determine it first:

$$n_a = (20.0 \text{ mL})(0.100 \text{ mmol}\cdot\text{mL}^{-1}) = 2.00 \text{ mmol H}_3\text{O}^{1+}$$

a) 10.0 mL of base

The number of moles of base: $(10.0 \text{ mL})(0.100 \text{ mmol}\cdot\text{mL}^{-1}) = 1.00 \text{ mmol OH}^{1-}$

The base is the limiting reactant ($n_b < n_a$), so the reaction table is

	$\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2\text{H}_2\text{O}$		
initial	2.00	1.00	mmol
Δ	-1.00	-1.00	mmol
eq	1.00	~0	mmol

The final solution is a strong acid solution containing 1.0 mmol of hydronium ions in a total volume of $20.0 + 10.0 = 30.0$ mL. The hydronium ion concentration and pH are

$$[\text{H}_3\text{O}^{1+}] = \frac{1.00 \text{ mmol}}{30.0 \text{ mL}} = 0.033 \text{ M} \quad \text{and} \quad \text{pH} = -\log(0.033) = 1.48$$

b) 20.0 mL of base

The number of moles of base: $(20.0 \text{ mL})(0.100 \text{ mmol}\cdot\text{mL}^{-1}) = 2.00 \text{ mmol OH}^{1-}$

The number moles of acid = the number of moles of base, so this is the equivalence point.

	$\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2\text{H}_2\text{O}$		
initial	2.00	2.00	mmol
Δ	-2.00	-2.00	mmol
eq	~0	~0	mmol

No excess acid or base is present, so the solution is pure water, which has a pH = 7.00.

Table 7.1 Solution type resulting from the reaction of n_a moles of a strong acid with n_b moles of a strong base

a) $n_a > n_b$	Strong acid solution with $[\text{H}_3\text{O}^{1+}] = \frac{n_a - n_b}{\text{total volume}}$
b) $n_a = n_b$	Water with pH = 7.00
c) $n_a < n_b$	Strong base solution with $[\text{OH}^{1-}] = \frac{n_b - n_a}{\text{total volume}}$

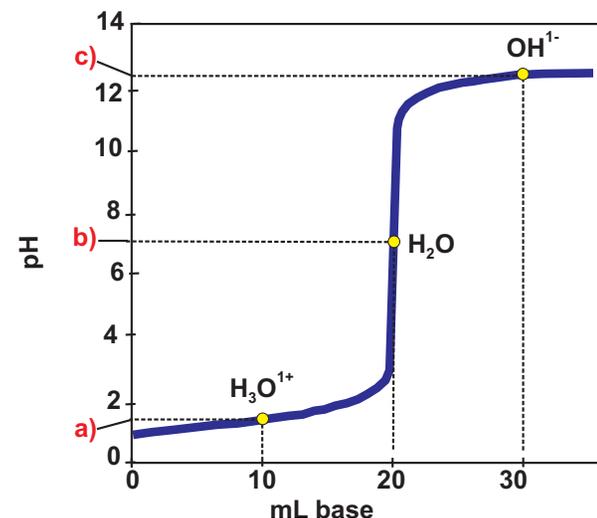


Figure 7.2 Strong acid-strong base titration curve.

Titration of 20.0 mL of 0.100 M HCl with 0.100 M NaOH. The equivalence point (yellow circle) in a strong acid-strong base titration is pure water, so the pH is 7.00. Points a, b, and c lie in regions a, b, and c of Table 7.1 and correspond to points a, b, and c in Example 7.10.

c) 30.0 mL of base

The number of moles of base: $(30.0 \text{ mL})(0.100 \text{ mmol}\cdot\text{mL}^{-1}) = 3.00 \text{ mmol OH}^{1-}$

The base is the limiting reactant ($n_a < n_b$), so the reaction table is

	$\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2\text{H}_2\text{O}$			
initial	2.00	3.00		mmol
Δ	-2.00	-2.00		mmol
eq	~0	1.00		mmol

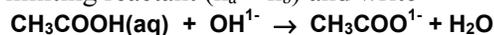
The concentration of the excess hydroxide and the resulting pH are

$$[\text{OH}^{1-}] = \frac{1.00 \text{ mmol}}{50.0 \text{ mL}} = 0.0200 \text{ M}$$

$$\text{pOH} = -\log(0.0200) = 1.70 \text{ and } \text{pH} = 14.00 - 1.70 = 12.30$$

WEAK ACID - STRONG BASE REACTIONS

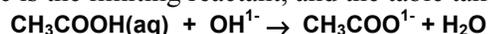
Consider the reaction of n_a moles of acetic acid with n_b moles of hydroxide ion. The reaction is the reverse of the K_b reaction of acetate ion, $K = (K_b)^{-1} = K_a/K_w = 1.8 \times 10^9$. The large value of K means that the limiting reactant essentially disappears. We consider the case where the acid is the limiting reactant ($n_a < n_b$) and write



initial	n_a	n_b	0	mol
Δ	- n_a	- n_a	+ n_a	mol
eq	~0	$n_b - n_a$	n_a	mol

The resulting solution contains $(n_b - n_a)$ moles of hydroxide ion and is, therefore, a solution of a strong base.* The acetate ion has no effect on the pH of the solution due to the common-ion effect exerted by the excess hydroxide ion.

When $n_b < n_a$, the base is the limiting reactant, and the table takes the following form:



initial	n_a	n_b	0	mol
Δ	- n_b	- n_b	+ n_b	mol
eq	$n_a - n_b$	~0	n_b	mol

The solution contains a weak acid and its conjugate base, so it is a buffer solution that contains $(n_a - n_b)$ moles of the weak acid and n_b moles of its conjugate base.† Thus, *adding a strong base to an excess of weak acid is another way to make a buffer solution.* Halfway to the equivalence point in the titration of a weak acid with a strong base, $n_b = \frac{1}{2} n_a$, so $n_b/(n_a - n_b) = 1$. $\log(1) = 0$, so $\text{pH} = \text{p}K_a + 0$ at that point. We conclude that

The pH at the midpoint of the titration (half-way to the equivalence point) of a weak acid and a strong base equals the $\text{p}K_a$ of the weak acid.

* Strong base: $[\text{OH}^{1-}] = \frac{n_b - n_a}{\text{total volume}}$ and $\text{pH} = 14.00 - \log[\text{OH}^{1-}]$.

† Buffer: $\text{pH} = \text{p}K_a + \log\left(\frac{n_b}{n_a - n_b}\right)$

n_a is the initial number of moles of acid. The equilibrium number of moles of acid is $n_a - n_b$, which was represented by n_a in Equation 7.2. n_b is the initial number of moles of strong base, but it is also the equilibrium number of moles of weak base that are produced.

At the equivalence point in a titration, $n_a = n_b$, so the reaction table becomes

	$\text{CH}_3\text{COOH} +$	OH^{1-}	\rightarrow	$\text{CH}_3\text{COO}^{1-} + \text{H}_2\text{O}$	
Initial	n_a	n_b		0	mol
Δ	$-n_a$	$-n_b$		$+n_b$	mol
Eq	~ 0	~ 0		n_b	mol

The solution in this case is that of a weak base containing n_b (or n_a) moles of the acetate ion. The solution types that can result from the reaction of a weak acid and a strong base are summarized in Table 7.2 and demonstrated in the titration curve in Example 7.11.

Example 7.11

Determine the pH at each of the following points in the titration curve for the titration of 20.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH (Figure 7.3).

The parts of this example correspond to Points a – d of Figure 7.3 and lie in the regions a – d that are defined in Table 7.2. First, determine the number of moles of acid:

$$n_a = (20.0 \text{ mL})(0.100 \text{ M}) = 2.00 \text{ mmol CH}_3\text{COOH}$$

a) 0 mL ($n_b = 0$)

No acid has been added, so the initial solution is a weak acid

$$[\text{H}_3\text{O}^{1+}] = \sqrt{K_a c_a} = \sqrt{(1.8 \times 10^{-5})(0.100)} = 1.3 \times 10^{-3} \text{ M and pH} = 2.87$$

b) 10.0 mL ($n_a > n_b$)

The number of moles of base added is

$$n_b = (10.0 \text{ mL})(0.100 \text{ M}) = 1.00 \text{ mmol OH}^{1-}$$

The base is the limiting reactant ($n_b < n_a$), so the reaction table is

	$\text{CH}_3\text{COOH} +$	OH^{1-}	\rightarrow	$\text{CH}_3\text{COO}^{1-} + \text{H}_2\text{O}$	
Initial	2.00	1.00		0	mmol
Δ	-1.00	-1.00		+1.00	mmol
Eq	1.00	~ 0		1.00	mmol

The result is a buffer solution containing 1.00 mmol of acetic acid and 1.00 mmol of its conjugate base. The second way to prepare a buffer is to add hydroxide ion to an excess of weak acid.

The $\text{p}K_a$ of acetic acid is $-\log(1.8 \times 10^{-5}) = 4.74$, so the pH is

$$\text{pH} = 4.74 + \log\left(\frac{1.00}{1.00}\right) = 4.74$$

$\log(1) = 0$, so $\text{pH} = \text{p}K_a$ when the equilibrium number of moles of the acid and its conjugate base are identical, which occurs half-way to the equivalence point. We conclude that **the pH at the midpoint of a titration of a weak acid and a strong base equals the $\text{p}K_a$ of the acid.**

Table 7.2 The type of solution resulting from the reaction of n_a moles of weak acid with n_b moles of a strong base

a) $n_b = 0$: Weak acid solution with n_a moles of acid.

$$[\text{H}_3\text{O}^{1+}] = \sqrt{K_a c_a}; c_a = \frac{n_a}{V}$$

b) $n_a > n_b$: Buffer solution with $n_a - n_b$ moles of acid and n_b moles of conjugate base: $\text{pH} = \text{p}K_a + \log\left(\frac{n_b}{n_a - n_b}\right)$

c) $n_a = n_b$: Weak base solution containing $n_b = n_a$ moles of the weak base $\text{pH} > 7$;

$$[\text{OH}^{1-}] = \sqrt{K_b c_b}; c_b = \frac{n_b}{\text{total volume}}$$

d) $n_a < n_b$: Strong base solution with $n_b - n_a$ moles of OH^{1-} .

$$[\text{OH}^{1-}] = \frac{n_b - n_a}{\text{total volume}} \text{ and } \text{pH} = 14.00 - \log[\text{OH}^{1-}]$$

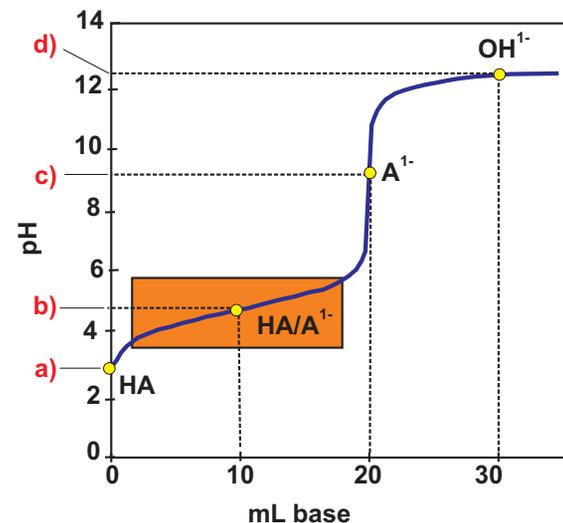


Figure 7.3 Weak acid-strong base titration curve

Titration of 20.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH. Points a – d lie in regions defined in Table 7.2 and correspond to Parts a – d in Example 7.11. The orange rectangle outlines the buffer range of the acetic acid/acetate ion buffer.

a) $n_b = 0$; a solution of the weak acid HA.

b) $n_b < n_a$; a buffer solution. Point b is the midpoint of the titration, so $\text{pH} = \text{p}K_a$, which is 4.74 for acetic acid.

c) $n_b = n_a$; the equivalence point is a solution of the weak base A^{1-} .

d) $n_b > n_a$; excess OH^{1-} makes the solution a strong base.

c) 20.0 mL ($n_a = n_b$)

$$n_b = (20.0 \text{ mL})(0.100 \text{ M}) = 2.00 \text{ mmol OH}^{1-}$$

$n_b = n_a$, so this is the equivalence point. The reaction table is

	CH_3COOH	$+$	OH^{1-}	\rightarrow	$\text{CH}_3\text{COO}^{1-}$	$+$	H_2O	
Initial	2.00		2.00		0			mmol
Δ	-2.00		-2.00		+2.00			mmol
Eq	~ 0		~ 0		2.00			mmol

The resulting solution is a **weak base** that contains 2.00 mmol of the base ($\text{CH}_3\text{COO}^{1-}$) in $20.0 + 20.0 = 40.0$ mL of solution. $K_b = 5.6 \times 10^{-10}$, so the hydroxide ion concentration is

$$[\text{OH}^{1-}] = \sqrt{K_b \times c} = \sqrt{(5.6 \times 10^{-10}) \left(\frac{2.00 \text{ mmol}}{40.0 \text{ mL}} \right)} = 5.3 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(5.3 \times 10^{-6}) = 5.28 \text{ and } \text{pH} = 14.00 - 5.28 = 8.72$$

d) 30.0 mL ($n_a < n_b$)

$$n_b = (30.0 \text{ mL})(0.100 \text{ mmol} \cdot \text{mL}^{-1}) = 3.00 \text{ mmol OH}^{1-}$$

The base is the limiting reactant ($n_a < n_b$), so the reaction table is

	CH_3COOH	$+$	OH^{1-}	\rightarrow	$\text{CH}_3\text{COO}^{1-}$	$+$	H_2O	
Initial	2.00		3.00		0			mmol
Δ	-2.00		-2.00		+2.00			mmol
Eq	~ 0		1.00		2.00			mmol

The excess hydroxide ion suppresses any reaction of acetate ion, so the solution is a **strong base** with the following concentration and pH:

$$[\text{OH}^{1-}] = \frac{1.00 \text{ mmol}}{50.0 \text{ mL}} = 0.0200 \text{ M}$$

$$\text{pOH} = -\log(0.0200) = 1.70 \text{ and } \text{pH} = 14.00 - 1.70 = 12.30$$

Note that the pH at this point is identical to the strong acid-strong base titration.

Example 7.12

The titration curve for the titration of 50.00 mL of an unknown acid with 0.122 M NaOH is shown in the margin. Determine the concentration and pK_a of the acid.

The concentration is determined from the equivalence point, which is at 60.65 mL of a 0.122 M base solution. Thus, the number of mmoles of base at the equivalence point is $n_b = (60.65 \text{ mL})(0.122 \text{ M}) = 7.40 \text{ mmol}$, which equals the number of mmoles of acid in 50 mL. Thus the concentration of the acid is

$$c_a = \frac{7.40 \text{ mmol}}{50.00 \text{ mL}} = 0.148 \text{ M}$$

PRACTICE EXAMPLE 7.5

What is the pH of a solution prepared by mixing 34.0 mL of 0.250 M NaOH and 16.5 mL of 0.515 M KHSO_4 ?

Reaction table:

Rxn:

in

Δ

eq

solution type: _____ solution volume: _____ mL

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

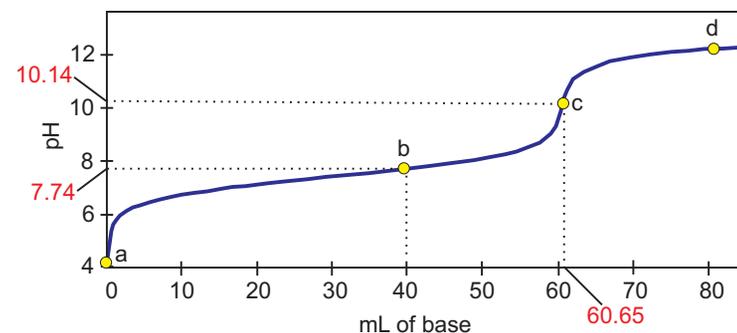
$$K_a \text{ of } \text{HSO}_4^{1-} = \text{_____} \text{ from Appendix C}$$

$$K_b \text{ of } \text{SO}_4^{2-} = \text{_____} = \text{_____}$$

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

$$\text{pOH} = \text{_____}$$

$$\text{pH} = \text{_____} = \text{_____}$$



Example 7.12

The pK_a of the acid is most easily determined from a pH in the buffer range. Indeed, the pK_a is near 7.5 as that is the approximate pH at the midpoint of the titration. We use the fact that $pH = 7.74$ at the 40 mL point to determine the pH more precisely. $n_a = 7.40$ mmol and $n_b = (40.00 \text{ mL})(0.122 \text{ M}) = 4.88$ mmol at this point, so the reaction table is

	HA(aq)	$+$	OH^{1-}	\rightarrow	A^{1-}	$+$	H_2O	
in	7.40		4.88		0			mmol
Δ	-4.88		-4.88		+4.88			mmol
eq	2.52		~0		4.88			mmol

Solve Equation 7.2 for the pK_a of a buffer solution that has a $pH = 7.74$ and contains 2.52 mmol acid and 4.88 mmol base and solve for pK_a .

$$pK_a = pH - \log\left(\frac{n_b}{n_a}\right) = 7.74 - \log\left(\frac{4.88}{2.52}\right) = 7.45$$

Polyprotic acids dissociate one proton at a time, and they are deprotonated by OH^{1-} ion one proton at a time. The loss of each proton gives rise to one equivalence point. The equilibrium constants for the individual dissociations are usually very different, so only one or two species usually have non-negligible concentrations in polyprotic acid solutions. Indeed, their equilibria are identical to those of monoprotic acids except that the base may be amphiprotic. Example 7.13 shows how to treat the reaction of a polyprotic acid with hydroxide ion and gives an example of a titration curve.

Example 7.13

Determine the pH at various points in the titration curve for the titration of 20.0 mL of 0.100 M H_2A ($pK_1 = 4.00$, $pK_2 = 9.00$) with 0.100 M NaOH shown in Figure 7.4.

There are two equivalence points: 20 mL and 40 mL. H_2A is the weak acid up to the first equivalence point, but HA^{1-} is the acid between the first and the second.

b) 10.0 mL

This is half-way to the first equivalence point, so $[\text{H}_2\text{A}] = [\text{HA}^{1-}]$ and $pH = pK_1 = 4.00$

c) 15.0 mL

$n_a = (20.0 \text{ mL})(0.100 \text{ M}) = 2.00$ mmol H_2A $n_b = (15.0 \text{ mL})(0.100 \text{ M}) = 1.50$ mmol OH^{1-}

	H_2A	$+$	OH^{1-}	\rightarrow	HA^{1-}	$+$	H_2O	$pK_1 = 4.00$
initial	2.00		1.50		0			mmol
Δ	-1.50		-1.50		+1.50			mmol
eq	0.50		~0		1.50			mmol

a buffer solution, so $pH = pK_1 + \log\left(\frac{\text{mol HA}^{1-}}{\text{mol H}_2\text{A}}\right) = 4.00 + \log\left(\frac{1.50}{0.50}\right) = 4.48$

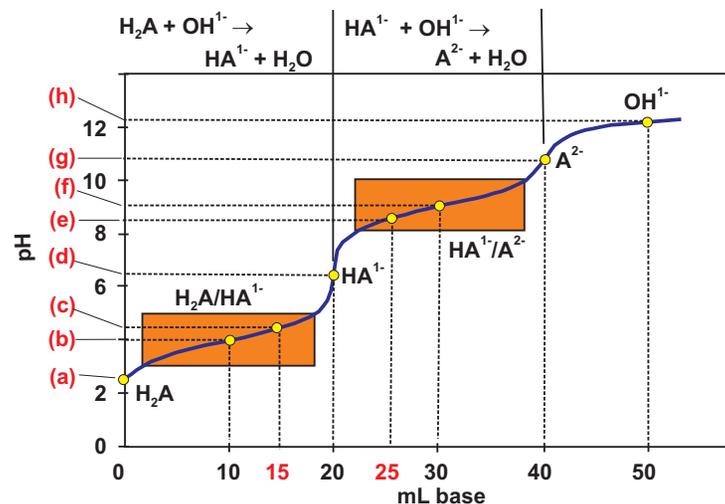


Figure 7.4 Diprotic acid-strong base titration curve

Titration of 20.0 mL of 0.100 M H_2A with 0.100 M NaOH. $pK_1 = 4.00$ and $pK_2 = 9.00$. The rectangles outline the two buffer ranges. See Example 7.13 for details of Points b - f.

- a) Solution of weak acid H_2A
- b & c) Buffer solution. Point b is half-way to the first equivalence point, so $pH = pK_1 = 4.00$.
- d) The first equivalence point is a solution of HA^{1-} , which is amphiprotic, so the pH of the solution is $\frac{1}{2}(pK_1 + pK_2) = 6.5$.
- e & f) Buffer solution. Point f is the midpoint between the first and second equivalence points, so $pH = pK_2 = 9.0$.
- g) The second equivalence point is a solution of A^{2-} , a weak base.
- h) Strong base solution that is characterized by the concentration of the excess hydroxide.

d) 20.0 mL

All of the H_2A has been converted to HA^{1-} at the equivalence point. HA^{1-} is an amphiprotic substance, so we use Equation 6.12 to determine the pH.

$$\text{pH} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) = \frac{1}{2}(4.00 + 9.00) = 6.50$$

e) 25.0 mL

This is after the first equivalence point, so the 2.00 mmol H_2A have been converted into 2.00 mmol HA^{1-} , which is now the reacting acid.

$$n_b = (25.0 \text{ mL})(0.100 \text{ M}) = 2.50 \text{ mmol OH}^{1-}$$

2.50 mmol OH^{1-} have been added, but 2.00 mmol were consumed in the reaction with H_2A to produce 2.00 mmol HA^{1-} . Thus, only 0.50 mmol OH^{1-} is available to react with HA^{1-} .

	HA^{1-}	$+$	OH^{1-}	\rightarrow	A^{2-}	$+$	H_2O	$\text{p}K_2 = 9.00$
initial	2.00		0.50		0		mmol	
Δ	-0.50		-0.50		+0.50		mmol	
eq	1.50		~0		0.50		mmol	

$$\text{pH} = \text{p}K_2 + \log\left(\frac{\text{mol A}^{2-}}{\text{mol HA}^{1-}}\right) = 9.00 + \log\left(\frac{0.50}{1.50}\right) = 8.52$$

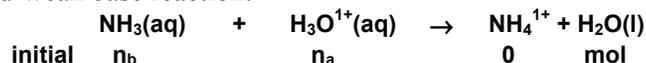
f) 30.0 mL

This is halfway between the first and second equivalence, so $\text{pH} = \text{p}K_2 = 9.00$

Note that the pH change at the two equivalence points in Figure 7.4 is less dramatic than for the monoprotic acid in Figure 7.3. This is to be expected because the pH range of the titrations are nearly the same ($\text{pH} = 2$ to 12), but the diprotic acid has two equivalence points while the monoprotic acid has only one.

STRONG ACID - WEAK BASE REACTIONS

We use the reaction of n_b moles of ammonia with n_a moles of HCl as our example of a strong acid-weak base reaction:



This reaction is the reverse of the K_a reaction for NH_4^{1+} , so $K = (K_a)^{-1} = (5.6 \times 10^{-10})^{-1} = 1.8 \times 10^9$. Using the same reasoning for this extensive reaction as in the reaction of a weak acid and a strong base, we obtain the results shown in Table 7.3. Note that when $n_a < n_b$, the result is a buffer. Thus, *adding a strong acid to an excess of weak base is the third way to make a buffer.*

Table 7.3 The type of solution resulting from the reaction of n_a moles of a strong acid with n_b moles of a weak base

- a) $n_a = 0$ A weak base: $[\text{OH}^{1-}] = \sqrt{K_b c_b}$; $\text{pH} = 14.00 - \log[\text{OH}^{1-}]$
- b) $n_a < n_b$ Buffer solution containing n_a moles of acid and $(n_b - n_a)$ moles of base: $\text{pH} = \text{p}K_a + \log\left(\frac{n_b - n_a}{n_a}\right)$
- c) $n_a = n_b$ Weak acid solution containing $n_b = n_a$ moles of the weak acid:
 $[\text{H}_3\text{O}^{1+}] = \sqrt{K_a c_a}$; $c_a = \frac{n_a}{\text{total volume}}$; $\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$
- d) $n_a > n_b$ Strong acid solution containing $n_a - n_b$ moles of H_3O^{1+}
 and $[\text{H}_3\text{O}^{1+}] = \frac{n_a - n_b}{\text{total volume}}$; $\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$

Example 7.14

Determine the pH at each of the following points in the titration curve for the titration of 20.0 mL of 0.100 M NH_3 with 0.100 M HCl.

The points are shown in Figure 7.5 and defined in Table 7.3. From Appendix C:

For NH_4^{1+} : $K_a = 5.6 \times 10^{-10}$ and $\text{p}K_a = 9.25$

a) 0 mL HCl ($n_a = 0$)

Prior to the addition of acid, the solution is one of NH_3 , which is a weak base.

$$[\text{OH}^{1-}] = \sqrt{K_b c_b}; \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{-5}$$

$$[\text{OH}^{1-}] = \sqrt{(1.8 \times 10^{-5})(0.100)} = 1.3 \times 10^{-3} \text{ M} \Rightarrow \text{pOH} = -\log(1.3 \times 10^{-3}) = 2.87$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.87 = 11.13$$

b) 10 mL ($n_a < n_b$)

$$n_a = (10.0 \text{ mL})(0.100 \text{ M}) = 1.00 \text{ mmol } \text{H}_3\text{O}^{1+}$$

The acid is the limiting reactant ($n_a < n_b$), so the reaction table is

	NH_3	H_3O^{1+}	\rightarrow	NH_4^{1+}	H_2O	
Initial	2.00	1.00		0		mmol
Δ	-1.00	-1.00		+1.00		mmol
Eq	1.00	~ 0		1.00		mmol

The result is a **buffer solution** containing 1.00 mmol of ammonia and 1.00 mmol of its conjugate acid. The $\text{p}K_a$ of the acid (NH_4^{1+}) is 9.25, so the pH is

$$\text{pH} = 9.25 + \log\left(\frac{1.00}{1.00}\right) = 9.25 \quad \text{This is the midpoint of the titration, so } \text{pH} = \text{p}K_a.$$

The third way to prepare a buffer is to add a strong acid to an **excess** of a weak base.

c) 20 mL ($n_a = n_b$)

$$n_a = (20.0 \text{ mL})(0.100 \text{ M}) = 2.00 \text{ mmol } \text{H}_3\text{O}^{1+}$$

$n_b = n_a$, so this is the equivalence point. The reaction table is

	NH_3	H_3O^{1+}	\rightarrow	NH_4^{1+}	H_2O	
Initial	2.00	2.00		0		mmol
Δ	-2.00	-2.00		+2.00		mmol
Eq	~ 0	~ 0		2.00		mmol

The resulting solution is a **weak acid** that contains 2.00 mmol of the acid (NH_4^{1+}) in 20.0 + 20.0 = 40.0 mL of solution. $K_a = 5.6 \times 10^{-10}$, so the hydronium ion concentration is

$$[\text{H}_3\text{O}^{1+}] = \sqrt{(5.6 \times 10^{-10})\left(\frac{2.00 \text{ mmol}}{40.0 \text{ mL}}\right)} = 5.3 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = -\log(5.3 \times 10^{-6}) = 5.28$$

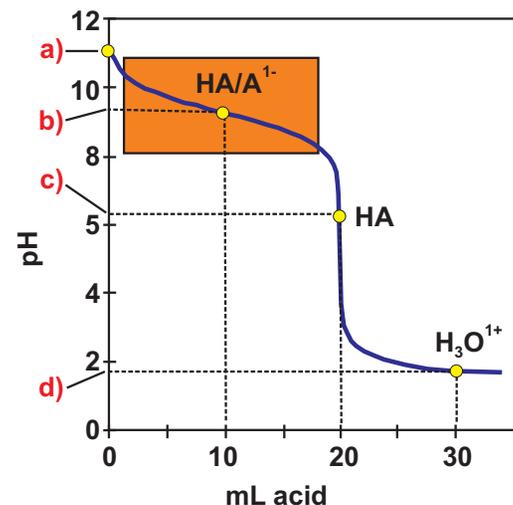


Figure 7.5 Weak-base-strong acid titration curve

Titration of 20.0 mL of 0.100 M NH_3 with 0.100 M HCl. See Example 7.14 for details on each point.

- a) $n_a = 0$ – a solution of the weak base NH_3
- b) $n_a < n_b$ – a buffer solution, Point b is the midpoint of the titration, so $\text{pH} = \text{p}K_a$, which is 9.25 for ammonium ion.
- c) $n_a = n_b$ – the equivalence point is a solution of the weak acid HA.
- d) $n_a > n_b$ – excess H_3O^{1+} makes the solution a strong acid.

d) 30 mL ($n_a > n_b$)

$$n_a = (30.0 \text{ mL})(0.100 \text{ mmol}\cdot\text{mL}^{-1}) = 3.00 \text{ mmol H}_3\text{O}^{1+}$$

The base is the limiting reactant ($n_a < n_b$), so the reaction table is

	$\text{NH}_3 +$	H_3O^{1+}	\rightarrow	$\text{NH}_4^{1+} + \text{H}_2\text{O}$	
Initial	2.00	3.00		0	mmol
Δ	-2.00	-2.00		+2.00	mmol
Eq	~0	1.00		2.00	mmol

The excess hydronium ion suppresses the reaction of ammonium ion with water, so the solution is a **strong acid** with the following concentration and pH:

$$[\text{H}_3\text{O}^{1+}] = \frac{1.00 \text{ mmol}}{50.0 \text{ mL}} = 0.0200 \text{ M} \quad \& \quad \text{pH} = -\log(0.0200) = 1.70$$

We have presented all three ways to make a buffer. In summary, they can be made by

- 1) adding the acid directly to its conjugate base,
- 2) adding a strong base to an excess of the weak acid, and
- 3) adding a strong acid to an excess of the weak base.

Example 7.15 demonstrates the second method.

Example 7.15

How many mL of 0.856 M HCl must be added to 250.0 mL of 0.116 M KClO to make a pH = 8.00 buffer? $\text{pK}_a = 7.46$ for HClO.

Set up the reaction table for the reaction of an unknown amount of acid with $n_b = (250 \text{ mL})(0.116 \text{ M}) = 29.0 \text{ mmol}$ of ClO^{1-} ion.

	$\text{ClO}^{1-} +$	H_3O^{1+}	\rightarrow	$\text{HClO} +$	H_2O
In	29.0	x		0	mmol
Δ	-x	-x		+x	mmol
Eq	29.0-x	~0		x	mmol

Use the Henderson-Hasselbalch equation with pH = 8.00, $\text{pK}_a = 7.46$, $n_b = 29.0 - x$ and $n_a = x$ to solve for x.

$$8.00 = 7.46 + \log\left(\frac{29.0-x}{x}\right) \quad \text{or} \quad \log\left(\frac{29.0-x}{x}\right) = 8.00 - 7.46 = 0.54$$

$$\frac{29.0-x}{x} = 10^{0.54} = 3.47 \quad \Rightarrow \quad x = \frac{29.0}{4.47} = 6.49 \text{ mmol H}_3\text{O}^{1+}$$

$$\text{Determine the volume of acid required: } 6.49 \text{ mmol} \times \frac{1 \text{ mL}}{0.856 \text{ mmol}} = 7.58 \text{ mL}$$

7.4 ACID-BASE COMPOSITION FROM EQUILIBRIUM pH

Solutions are frequently prepared by adjusting the solution pH to a desired level rather than adding a known volume of acid or base. For example, the easiest way to make a buffer of a desired pH is to decide on the proper acid-base pair, make a solution that contains an appreciable amount of the acid or base and then add a strong base or acid until the solution has the required pH. The question then becomes: Once you have attained the appropriate pH, what are the concentrations of the acid(s) and base(s) in the solution?

One equation is required for each unknown concentration in a solution, so determining $[H_2X]$, $[HX^1]$, and $[X^2]$ in a solution of a diprotic acid involves three equations and three unknowns. The equilibrium constant expressions for K_1 and K_2 are two of the equations. The third equation is mass balance: $c_o = [H_2X] + [HX^1] + [X^2]$. Fortunately, chemistry can usually be used to simplify the algebra because only one or two of the concentrations are usually appreciable at any pH. Once the one or two appreciable concentrations have been determined at a given pH, the other concentrations can be readily determined from the given K 's, c_o , and pH. Thus, our first task is to identify these one or two species that dominate the concentration. We do so by assuming that the concentration of a substance is negligible if it is less than 1% of the concentration of either its conjugate acid or base.* Thus, the acid concentration is negligible if $[base]/[acid] > 100$, and the base concentration is negligible if $[base]/[acid] < 0.01$. The pH at which each ratio is achieved can be determined with Equation 7.2. Thus, the acid is negligible if $pH > pK_a + \log(100) = pK_a + 2$, and the base is negligible if $pH < pK_a + \log(0.01) = pK_a - 2$. We conclude that *the concentration of an acid and its conjugate base are both appreciable at pH's within 2 pH units of the pK_a of the acid, but only the acid can be appreciable below this pH range, and only the base can be appreciable above it.*

For example, consider the case of acetic acid in Figure 7.6. The pK_a of CH_3COOH is 4.7, so $[CH_3COOH] = c_o$ if $pH < 2.7$ ($pH = 4.7 - 2$), but $[CH_3COO^1] = c_o$ if $pH > 6.7$ ($4.7 + 2$). At intermediate pH values ($2.7 < pH < 6.7$), neither concentration is negligible, so we use $[CH_3COOH] + [CH_3COO^1] = c_o$. Figure 7.7 shows the concentrations in an H_2S ($pK_1 = 7.0$, $pK_2 = 12.9$) solution. The two yellow boxes represent the two pH ranges ($pK_a \pm 2$) in which both the acid (H_2S or HS^1) and its conjugate base (HS^1 or S^2) are appreciable. Only one substance is appreciable at all other pH values. The example of a triprotic acid, H_3PO_4 , is examined in Example 7.16. Even though there are four concentrations to determine, no more than two are appreciable at any pH.

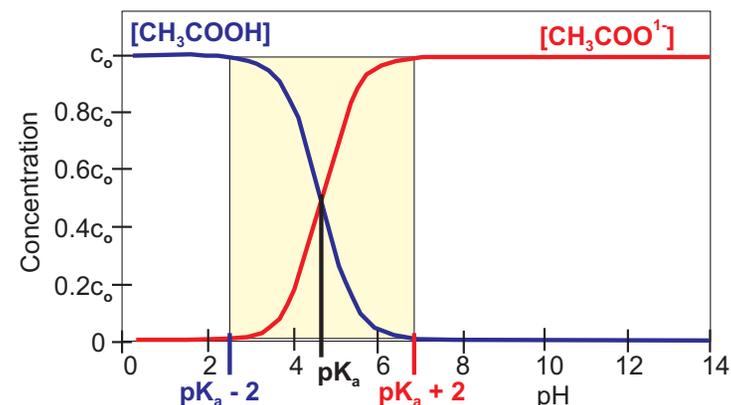


Figure 7.6 Concentrations in acetic acid as a function of pH

The $[acid] \sim c_o$ and $[base] \sim 0$ at pH's below ($pK_a - 2$), but $[acid] \sim 0$ and $[base] \sim c_o$ at pH's above ($pK_a + 2$). The concentrations of both substances are appreciable only in the yellow region. $pK_a = 4.74$

* Recall from Chapter 6 that we used the 5% rule, which stated that a concentration was negligible if it was less than 5% of its conjugate acid or base concentration, so a 1% cut-off is somewhat arbitrary.

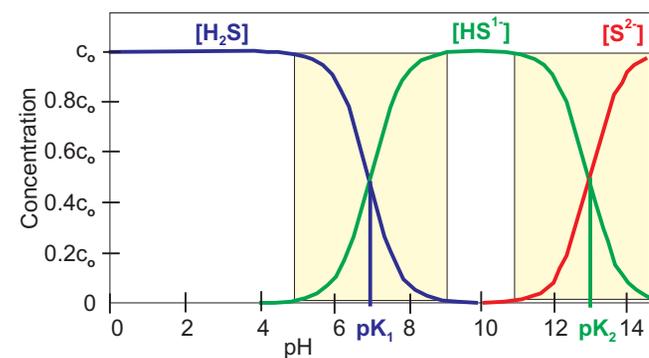
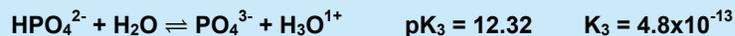
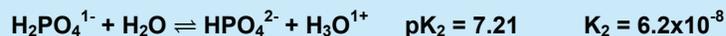


Figure 7.7 Concentrations in an H_2S solution as a function of pH

The concentrations of two substances are comparable and appreciable in the yellow boxes, but only one component is appreciable outside. The pH ranges of the yellow boxes are from $pH = pK_a - 2$ to $pH = pK_a + 2$.

Example 7.16

Solid NaOH is dissolved in a 0.10 M H_3PO_4 solution. Assume no volume change and calculate the concentrations of the phosphorus containing species at each pH.



a) pH = 7.0

pH = 7.0 is within 2 units of $\text{p}K_2$, so, in agreement with Figure 7.8, the concentrations of both the acid ($\text{H}_2\text{PO}_4^{1-}$) and the base (HPO_4^{2-}) in the K_2 equilibrium are appreciable. If $[\text{H}_2\text{PO}_4^{1-}] = x$, then $[\text{HPO}_4^{2-}] = 0.10 - x$. $[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 1.0 \times 10^{-7}$ M. Writing the K_2 expression and solving it for x , we obtain the following:

$$\frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_2\text{PO}_4^{1-}]} = \frac{(0.10 - x)(1.0 \times 10^{-7})}{x} = 6.2 \times 10^{-8}$$

$$\frac{(0.10 - x)}{x} = \frac{6.2 \times 10^{-8}}{1.0 \times 10^{-7}} = 0.62, \text{ so } x = \frac{0.10}{1.62} = 0.062 \text{ M} = [\text{H}_2\text{PO}_4^{1-}]$$

$$[\text{HPO}_4^{2-}] = 0.100 - 0.062 = 0.038 \text{ M}$$

Use $[\text{H}_2\text{PO}_4^{1-}] = 0.062$ M and $[\text{H}_3\text{O}^{1+}] = 1.0 \times 10^{-7}$ M in K_1 to obtain $[\text{H}_3\text{PO}_4]$.

$$\frac{[\text{H}_2\text{PO}_4^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_3\text{PO}_4]} = \frac{(0.062)(1.0 \times 10^{-7})}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3}$$

$$[\text{H}_3\text{PO}_4] = \frac{(0.062)(1.0 \times 10^{-7})}{7.5 \times 10^{-3}} = 8.3 \times 10^{-7} \text{ M}$$

Use the $[\text{HPO}_4^{2-}] = 0.038$ M and $[\text{H}_3\text{O}^{1+}] = 1.0 \times 10^{-7}$ M in K_3 to obtain $[\text{PO}_4^{3-}]$.

$$\frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^{1+}]}{[\text{HPO}_4^{2-}]} = \frac{[\text{PO}_4^{3-}](1.0 \times 10^{-7})}{0.038} = 4.8 \times 10^{-13}$$

$$[\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(0.038)}{1.0 \times 10^{-7}} = 1.8 \times 10^{-7} \text{ M}$$

b) pH = 10.0

pH = 10 is not within 2 units of any $\text{p}K_a$, so the concentration of only one species is appreciable at this pH. The pH lies between $\text{p}K_2$ and $\text{p}K_3$, so the dominant species is the one that is common to both the K_2 and K_3 equilibria. We conclude that $[\text{HPO}_4^{2-}] = c_0 = 0.10$ M at pH = 10. Again this is consistent with Figure 7.8.

We use $[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 1.0 \times 10^{-10}$ M and $[\text{HPO}_4^{2-}] = 0.10$ M in the K_2 and K_3 equilibria to obtain the concentrations of the conjugate acid and base of HPO_4^{2-} .

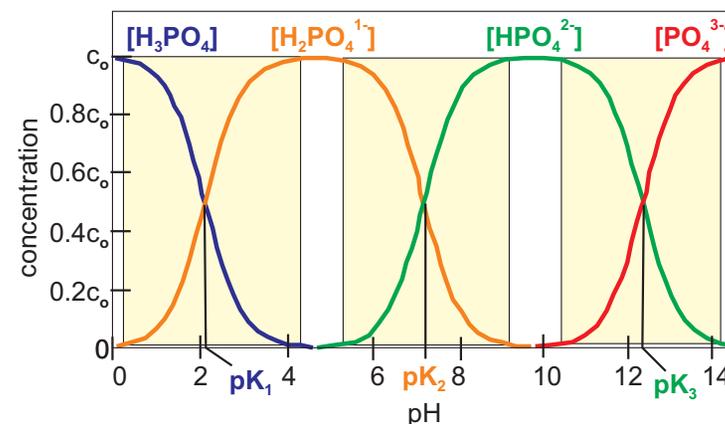


Figure 7.8 Phosphoric acid composition versus pH

See Example 7.14 for details. $\text{p}K_1 = 2.12$; $\text{p}K_2 = 7.21$; $\text{p}K_3 = 12.32$

Obtain $[\text{PO}_4^{3-}]$ from the K_3 equilibrium.

$$\frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^{1+}]}{[\text{HPO}_4^{2-}]} = \frac{[\text{PO}_4^{3-}](1.0 \times 10^{-10})}{0.10} = 4.8 \times 10^{-13}$$

$$[\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(0.10 \text{ M})}{1.0 \times 10^{-10}} = 4.8 \times 10^{-4} \text{ M}$$

Obtain $[\text{H}_2\text{PO}_4^{1-}]$ from the K_2 equilibrium.

$$\frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_2\text{PO}_4^{1-}]} = \frac{(0.10 \text{ M})(1.0 \times 10^{-10})}{[\text{H}_2\text{PO}_4^{1-}]} = 6.2 \times 10^{-8}$$

$$[\text{H}_2\text{PO}_4^{2-}] = \frac{(0.10 \text{ M})(1.0 \times 10^{-10})}{6.2 \times 10^{-8}} = 1.6 \times 10^{-4} \text{ M}$$

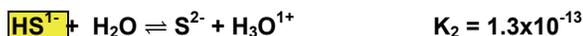
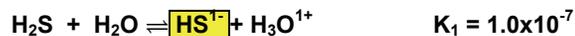
Use $[\text{H}_2\text{PO}_4^{1-}] = 1.6 \times 10^{-4} \text{ M}$ in the K_1 equilibrium to obtain $[\text{H}_3\text{PO}_4]$.

$$\frac{[\text{H}_2\text{PO}_4^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_3\text{PO}_4]} = \frac{(1.6 \times 10^{-4})(1.0 \times 10^{-10})}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3}$$

$$[\text{H}_3\text{PO}_4] = \frac{(1.6 \times 10^{-4})(1.0 \times 10^{-10})}{7.5 \times 10^{-3}} = 2.1 \times 10^{-12} \text{ M}$$

It should be noted that, while the concentrations in Example 7.16 were determined for a solution formed by adding NaOH to H_3PO_4 , the compositions at a given pH would be identical if the solutions had been prepared by adding a strong acid to PO_4^{3-} .

While the protons of a polyprotic acid are removed individually, the individual equilibria can be combined to eliminate concentrations of intermediate ions. For example, consider the dissociation equilibria of H_2S .



Note that the HS^{1-} ion cancels in the sum, so adding the two equations produces a chemical equation without HS^{1-} . The new chemical equation is the result of adding two equations, so its equilibrium constant equals the product of the equilibrium constants of the added reactions. K_{12} does not include $[\text{HS}^{1-}]$, so its use affords us a quick way to determine the concentration of sulfide ion in a solution where $[\text{H}_3\text{O}^{1+}]$ and $[\text{H}_2\text{S}]$ are known. However, $[\text{H}_2\text{S}]$ is the *equilibrium* concentration of H_2S , not its makeup

PRACTICE EXAMPLE 7.6

What are the H_2SO_3 , HSO_3^{1-} , and SO_3^{2-} concentrations in a 0.100 M H_2SO_3 ($\text{p}K_1 = 1.82$ and $\text{p}K_2 = 7.00$) solution at the following pH's?

a) pH = 5.0

Major component(s) in solution: _____

Concentration(s) of major component(s):

Concentration(s) of other component(s):

b) pH = 8.0

Major component(s) in solution: _____

Concentration(s) of major component(s):

Concentration(s) of other component(s):

concentration. If the pH is low enough that only a negligible amount of H_2S reacts then $[\text{H}_2\text{S}] = c_0$, but such is not the case at higher pH. When determining a pH with K_{12} , you should always check that $[\text{HS}^{1-}]$ is negligible at that pH.

Example 7.17

Sulfide ion is used to selectively precipitate metal ions from solution, but the concentration of the sulfide ion must be adjusted carefully to select which metals will precipitate. This is done by adjusting the pH of the solution.

a) What is $[\text{S}^{2-}]$ in a saturated solution of H_2S (0.10 M) at a pH = 3.0?

H_2S is not deprotonated at pH values less than $\text{p}K_a - 2 = 7.00 - 2 = 5.00$ (also see Figure 7.7), so $[\text{H}_2\text{S}] = 0.10$ M at pH = 3.0. We use the equilibrium constant for the combined equations to solve for $[\text{S}^{2-}]$.

$$[\text{S}^{2-}] = \frac{K_{12}[\text{H}_2\text{S}]}{[\text{H}_3\text{O}^{1+}]^2} = \frac{(1.3 \times 10^{-20})(0.10)}{(1.0 \times 10^{-3})^2} = 1.3 \times 10^{-15} \text{ M}$$

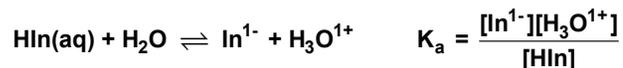
b) At what pH will the sulfide ion concentration be 1.0×10^{-12} M?

$$[\text{H}_3\text{O}^{1+}] = \sqrt{\frac{K_{12}[\text{H}_2\text{S}]}{[\text{S}^{2-}]}} = \sqrt{\frac{(1.3 \times 10^{-20})(0.10)}{(1.0 \times 10^{-12})}} = 3.6 \times 10^{-5} \text{ M} \Rightarrow \text{pH} = 4.44$$

pH = 4.44 < 5.0 ($\text{p}K_a - 2$), so H_2S is not deprotonated at this pH, $[\text{HS}^{1-}]$ is negligible, and the assumption that $[\text{H}_2\text{S}] = 0.10$ M is valid. ✓

7.5 ACID-BASE INDICATORS

Indicators are organic dyes that are also weak acids. They function as acid-base indicators because the weak acid (HIn) and its conjugate base (In^{1-}) differ in color. Consider the K_a of the indicator HIn :



The base to acid ratio in solution varies with the pH as shown below (Equation 7.3):

$$\frac{[\text{In}^{1-}]}{[\text{HIn}]} = \frac{K_a}{[\text{H}_3\text{O}^{1+}]} = K_a \times 10^{\text{pH}}$$

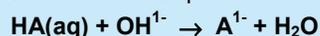
The human eye perceives the color of In^{1-} if this ratio is greater than 10 and the color of HIn if the ratio is less than 0.1. In order to change the ratio from 0.1 to 10, the hydronium ion concentration must decrease by a factor of 100, which means that the pH must increase by 2 pH units. For this reason, most indicators have a useful range of about 2 pH units.

Ideally, $[\text{HIn}] \sim [\text{In}^-]$ at the equivalence point so, a *good indicator* has a K_a that is close to the hydronium ion concentration at the equivalence point. Alternatively, a good indicator has a $\text{p}K_a$ that is close to the pH at the equivalence point. Table 7.4 gives the useful range of a series of common acid-base indicators.

Example 7.18

- a) What is the molarity of a weak monoprotic acid HA if 25.00 mL of the acid require 35.22 mL of 0.1095 M NaOH to reach the equivalence point?

Determining the concentration of an acid or base is the most common application of a titration. This example involves the reaction of a strong acid and a strong base:



$$n_b = 35.22 \text{ mL base} \times \frac{0.1095 \text{ mmol OH}^{1-}}{\text{mL base}} = 3.857 \text{ mmol OH}^{1-}$$

The equivalence point is that point where the number of moles of base that is added equals the number of moles of acid in the original sample, so 3.857 mmol HA were present in the original 25.00 mL.

$$\text{Molarity of acid} = \frac{3.857 \text{ mmol acid}}{25.00 \text{ mL solution}} = 0.1543 \text{ M}$$

- b) What is the K_a of the acid if the pH of the solution was 5.26 after the addition of 20.00 mL of the base?

$(20.00 \text{ mL})(0.1095 \text{ M}) = 2.190 \text{ mmol OH}^{1-}$, and the reaction table for the reaction of 2.190 mmol OH^{1-} with 3.857 mmol HA is

	HA(aq)	+ OH ¹⁻	→	A ¹⁻	+ H ₂ O	
in	3.857	2.190		0		mmol
Δ	-2.190	-2.190		+2.190		mmol
fin	1.667	~0		2.190		mmol

The solution contains appreciable amounts of both the acid and the base, so $\text{pH} = \text{p}K_a + \log(n_b/n_a)$. We are given the pH and have determined n_a and n_b , so we solve for the $\text{p}K_a$.

$$\text{p}K_a = \text{pH} - \log\left(\frac{n_b}{n_a}\right) = 5.26 - \log\left(\frac{2.190}{1.667}\right) = 5.14$$

Table 7.4 The pH range and color change of selected acid-base indicators

Indicator	pH range	color change
Methyl violet	1.0-1.6	yellow → blue
Thymol blue	1.2-2.8	red → yellow
Methyl orange	3.2-4.4	red → yellow
Bromocresol green	3.8-5.4	yellow → blue
Alizarin	5.4-6.6	colorless → yellow
Bromothymol blue	6.0-7.6	yellow → blue
Phenolphthalein	8.2-10.0	colorless → pink
Alizarin yellow R	10.1-12.0	yellow → red

PRACTICE EXAMPLE 7.7

An old sample of KHSO_4 is analyzed by dissolving 438.7 mg in ~50 mL of water and titrating the solution with 0.08221 M KOH. The endpoint was reached after the addition of 36.42 mL of the base. What is the percent purity of the KHSO_4 ?

Titration reaction:

$$\text{mmol OH}^{1-} \text{ added} = \quad = \quad \text{mmol}$$

$$\text{mmol of HSO}_4^{1-} \text{ in sample} = \quad \text{mmol}$$

$$\text{molar mass of KHSO}_4 = \quad \text{g} \cdot \text{mol}^{-1}$$

$$\text{mass of KHSO}_4 \text{ in sample:} \quad = \quad \text{mg}$$

percent purity of sample:

$$\% = \quad \times 100\% = \quad \%$$

c) What is the pH at the equivalence point?

The solution at the equivalence point has a volume of $25.00 + 35.22 = 60.22$ mL and it contains 3.857 mmol A^{1-} .

$$[A^{1-}] = \frac{3.857 \text{ mmol}}{60.22 \text{ mL}} = 0.06405 \text{ M}$$

$$pK_b = 14.00 - 5.14 = 8.86; K_b = 10^{-8.86} = 1.38 \times 10^{-9}$$

If we assume a negligible reaction of the base with water to produce OH^{1-} ,

$$[OH^{1-}] = \sqrt{(K_b)(c_o)} = \sqrt{(1.38 \times 10^{-9})(0.06405)} = 9.40 \times 10^{-6} \text{ M}$$

$[OH^{1-}]/[A^{1-}] = 1.5 \times 10^{-4}$, which is much less than 5%, so the assumption is valid. ✓

$$pH = 14.00 - \log[OH^{1-}] = 14.00 - \log(9.40 \times 10^{-6}) = 8.97$$

d) What indicator from Table 7.4 should be used to indicate the end point?

The best indicator from Table 7.4 to use at $pH \sim 9$ is phenolphthalein.

7.6 CHAPTER SUMMARY AND OBJECTIVES

Buffers are solutions of a weak acid and its conjugate base in comparable and appreciable amounts. They must be in comparable amounts to be effective. The effective buffer range is $0.10 < c_a/c_b < 10$. They must be present in appreciable amounts to have a good buffer capacity. Buffered solutions resist changes in pH brought on by the addition of either acid or base because the weak acid reacts with additional strong base while the weak base reacts with any additional strong acid. The result is the strong acid or base is converted into a weak base or acid.

One of five types of solutions result when acids and bases are mixed. The five types of solutions and how they are treated are as follows:

1. Strong acid solutions: $[H_3O^{1+}] = c_o$
2. Strong base solutions: $[OH^{1-}] = c_o$
3. Weak acid solution: $[H_3O^{1+}] = \sqrt{K_a c_o}$ (assumes very little reaction, so the equilibrium concentration of the weak acid = c_o)
4. Weak base solution: $[OH^{1-}] = \sqrt{K_b c_o}$ (assumes very little reaction, so the equilibrium concentration of the weak base = c_o)
5. Buffer solutions: $[H_3O^{1+}] = [H_3O^{1+}] = K_a \left(\frac{c_a}{c_b} \right)$ or $pH = pK_a + \log \left(\frac{c_b}{c_a} \right)$ (c_A and c_B are the makeup concentrations or number of moles of the acid and the base, respectively)

ANSWERS TO PRACTICE EXAMPLES

- 7.1 $pH = 3.80$
- 7.2 a) 3.31 b) 3.88 c) 2.80
- 7.3 NH_4^{1+}/NH_3 ; 0.39 mol NH_3 or
 HCO_3^{1-}/CO_3^{2-} ; 0.033 mol CO_3^{2-} or
 HCN/CN^{1-} ; 0.28 mol CN^{1-}
- 7.4 $[NO_2^{1-}] = 0.021 \text{ M}$
- 7.5 $[SO_4^{2-}] = 0.17 \text{ M}$ $pH = 7.58$
- 7.6 a) $[HSO_3^{1-}] = 0.10 \text{ M}$; $[H_2SO_3] = 6.7 \times 10^{-5} \text{ M}$; $[SO_3^{2-}] = 1.0 \times 10^{-3} \text{ M}$
 b) $[HSO_3^{1-}] = 0.0091 \text{ M}$; $[SO_3^{2-}] = 0.091 \text{ M}$; $[H_2SO_3] = 6.1 \times 10^{-9} \text{ M}$
- 7.7 92.94%

A titration curve is a plot of the pH of a solution as a function of the amount of titrant added. Titration curves are flat in buffer regions, but undergo dramatic pH changes near the equivalence points. There is one equivalence point for each acidic proton in the acid. The composition of an acid-base mixture at a given pH can be determined by comparing the pH with the pK_a values of the acid. If the pH is within 1.5 units of the pK_a , then both the acid and base are present in appreciable amounts, but if the pH is not within 1.5 units of a pK_a only one substance is present in appreciable amounts.

After studying the material presented in this chapter, you should be able to:

1. explain the common-ion effect and predict the effect of a common ion on an equilibrium mixture (Section 7.1);
2. define a buffer and explain how it works (Section 7.2);
3. choose an appropriate conjugate acid-base pair to use in the preparation of a buffer of a known pH (Section 7.2);
4. determine the base to acid ratio required to produce a buffer of a given pH (Section 7.2);
5. determine the pH of a buffer given the amounts of acid and base present (Section 7.2);
6. calculate the change in pH expected when a strong acid or base is added to a buffered solution (Section 7.2);
7. write acid-base reactions and determine their equilibrium constants from the K_a 's of the reacting and produced acids (Section 7.3);
8. determine the concentrations of all species in a solution prepared by mixing a strong acid (or base) with a strong base (or acid) or a weak base (or acid) (Section 7.3);
9. describe the three ways in which buffers can be made (Section 7.3);
10. define a titration curve and explain how it is determined (Section 7.3);
11. discuss how a titration curve varies with acid and base strengths (Section 7.3);
12. determine the pH at any point in the titration of a strong acid with a strong base, or a weak acid and a strong base, or a weak base and a strong acid (Section 7.3);
13. determine the concentrations of all species in an acid-base mixture given the initial concentration of the acid and the pH of the solution (Section 7.4);
14. describe the function of an indicator (Section 7.5); and
15. choose an indicator that is appropriate for a titration (Section 7.5).

7.7 EXERCISES

THE COMMON-ION EFFECT AND BUFFERS

1. What is a common ion and what is the common-ion effect?
2. Why can the dissociation of a weak base be ignored when calculating the pH of a solution that contains both a weak base and a strong base?
3. What is a buffer and how does it function?
4. Explain why the terms *appreciable* and *comparable* appear in the definition of a buffer.
5. Why is a solution that is 1.4 mM HF and 6.4 mM KF not a good buffer?
6. Why is a solution that is 1.3 M HF and 1.3 mM KF not a good buffer?
7. Explain why a solution of a strong acid and its conjugate base is not a buffer. Use a solution of HCl and KCl as an example.
8. Explain why a solution that is prepared by dissolving 0.1 mol of each of KH_2PO_4 and K_3PO_4 in 1 L of water is not a buffered solution.
9. Use Appendix C to determine the best acid/base pair to prepare buffers at the following pH's:
 - a) pH = 1.5
 - b) pH = 7.0
 - c) pH = 12.0
10. Select an acid-base pair from Appendix C that could be used to buffer a solution at each of the following pH's:
 - a) pH = 3.5
 - b) pH = 8.0
 - c) pH = 10.6
11. What is the pH of a solution that is 0.16 M NH_3 and 0.43 M NH_4Cl ?
12. What is the pH of a solution that is 0.21 M K_2HPO_4 and 0.096 M K_3PO_4 ?
13. What is the pH of a solution made by dissolving 7.6 g KNO_2 to 750 mL of 0.11 M HNO_2 ?
14. What is the pH of a solution made by dissolving 8.5 g of K_2CO_3 and 6.9 g KHCO_3 in 500 mL of water?
15. How many grams of potassium acetate must be added to 2.5 L of 0.250 M acetic acid to prepare a pH = 4.26 buffer?
16. How many grams of ammonium chloride must be added to 0.75 L of 1.2 M ammonia to prepare a pH = 10.18 buffer?
17. How many milliliters of 6.0 M NaOH must be added to 0.50 L of 0.20 M HNO_2 to prepare a pH = 3.86 buffer?
18. How many milliliters of 3.5 M HCl must be added to 3.8 L of 0.18 M K_2HPO_4 to prepare a pH = 7.42 buffer?

EQUILIBRIUM CONSTANTS FOR ACID BASE REACTIONS

19. Use the data in Appendix C to determine the equilibrium constants for the following reactions:
 - a) $\text{NH}_3(\text{aq}) + \text{HCN}(\text{aq}) \rightleftharpoons \text{NH}_4^{1+} + \text{CN}^{1-}$
 - b) $\text{S}^{2-} + \text{HCN}(\text{aq}) \rightleftharpoons \text{HS}^{1-} + \text{CN}^{1-}$
 - c) $\text{F}^{1-} + \text{HCN}(\text{aq}) \rightleftharpoons \text{HF}(\text{aq}) + \text{CN}^{1-}$
20. Use the data in Appendix C to determine the equilibrium constants for the following reactions:
 - a) $\text{NH}_3(\text{aq}) + \text{H}_3\text{O}^{1+} \rightleftharpoons \text{NH}_4^{1+} + \text{H}_2\text{O}$
 - b) $\text{F}^{1-} + \text{H}_2\text{O} \rightleftharpoons \text{HF}(\text{aq}) + \text{OH}^{1-}$
 - c) $\text{HSO}_3^{1-} + \text{HS}^{1-} \rightleftharpoons \text{H}_2\text{S}(\text{aq}) + \text{SO}_3^{2-}$

MIXING PROBLEMS

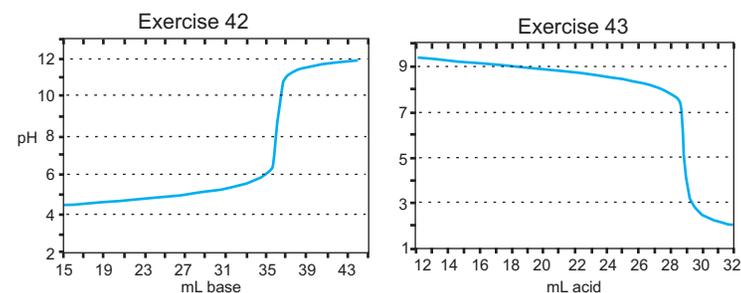
21. What is the sulfite ion concentration in a solution prepared by mixing 25.0 mL of 0.100 M H_2CO_3 and 25.0 mL of 0.100 M K_2SO_3 ?
22. What is the HOCl concentration in a solution prepared by mixing 50.0 mL of 0.160 M KOCl and 50.0 mL of 0.160 M NH_4Cl ?
23. What is the fluoride ion concentration in a solution prepared by mixing 25 mL of 0.16 M HF and 42 mL of 0.086 M KCN?
24. What is the ammonium ion concentration in a solution prepared by mixing 75 mL of 0.34 M ammonia and 85 mL of 0.18 M acetic acid?
25. What is the pH of a solution made by mixing 5.0 mL of 1.2 M HCl and 3.0 mL of 0.88 M HBr?
26. What is the pH of a solution prepared by mixing 39 mL of 0.074 M $\text{Ba}(\text{OH})_2$ and 57 mL of 0.11 M KOH?
27. What is the pH of a solution prepared by mixing 5.00 mL of 1.20 M HCl and 4.60 mL of 0.840 M NaOH?
28. What is the pH of a solution prepared by mixing 38.64 mL of 0.8862 M HCl and 53.66 mL of 0.7500 M NaOH?
29. Calculate the pH change that results when 10. mL of 3.0 M NaOH is added to 500. mL of each of the following solutions:
 - a) pure water
 - b) 0.10 M $\text{CH}_3\text{COO}^{1-}$
 - c) 0.10 M CH_3COOH
 - d) a solution that is 0.10 M in each $\text{CH}_3\text{COO}^{1-}$ and CH_3COOH

30. Calculate the pH change that results when 10. mL of 3.0 M HCl is added to 500. mL of each of the solutions in Exercise 29.
31. Calculate the pH change that results when 10. mL of 6.0 M HCl is added to 750. mL of each of the following solutions:
- pure water
 - 0.10 M NH_4Cl
 - 0.10 M NH_3
 - a solution that is 0.10 M in each NH_4^{1+} and NH_3
32. Calculate the pH change that results when 10. mL of 6.0 M NaOH is added to each of the solutions described in Exercise 31.

TITRATIONS

33. Sketch the titration curve for the titration of 50 mL of 0.1 M HA ($K_a = 10^{-7}$) with 0.1 M NaOH. What are the initial pH, the pH at the midpoint of the titration, and the pH at the equivalence point?
34. Sketch the titration curve for the titration of 50 mL of 0.1 M A^{-1} ($K_b = 10^{-7}$) with 0.1 M HCl. What are the initial pH, the pH at the midpoint of the titration, and the pH at the equivalence point?
35. What are the pH's of the first and second equivalence points in the titration of 25 mL of 0.080 M H_3PO_4 with 0.065 M NaOH?
36. What are the pH's of the two equivalence points in the titration of 25 mL of 0.080 M H_2CO_3 with 0.10 M NaOH?
37. Consider the titration of 35.0 mL of 0.122 M ammonia with 0.0774 M HCl.
- How many mL of HCl are required to reach the equivalence point?
 - What is the pH at the equivalence point? What indicator should be used for this titration?
 - What is the pH of the solution after addition of 15.0 mL of acid?
 - What is the pH of the solution after the addition of 65.0 mL of acid?
38. The CO_2 we breathe reacts with water in our blood to form the weak acid H_2CO_3 . What mole ratio of $\text{H}_2\text{CO}_3/\text{HCO}_3^{-1}$ is required to obtain a pH of 7.40, the pH of blood? Use $K_a = 4.4 \times 10^{-8}$ for H_2CO_3 .
39. 50.0 ml of 0.10 M HCl are required to titrate 10.0 ml of ammonia window cleaner to the end point.
- What is the concentration of ammonia in the window cleaner?
 - What is the pH of the window cleaner if $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$?
 - What is the pH at the equivalence point of the titration?
 - Which indicator in Table 7.4 would be the best to indicate the endpoint?

40. 5.182-g of a solid, weak, monoprotic acid is used to make a 100.0 mL solution. 25.00 mL of the resulting acid solution is then titrated with 0.09685 M NaOH. The pH after the addition of 20.00 mL of the base is 5.58, and the endpoint is reached after the addition of 47.92 mL of the base.
- How many moles of acid were present in the 25.00 mL sample?
 - What is the molar mass of the acid?
 - What is the pK_a of the acid?
41. A benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) sample was analyzed by dissolving 406.2 mg of the sample in 50 mL of water and titrating it with 0.06642 M NaOH.
- What is the percent purity of the benzoic acid if the titration required 38.62 mL of base?
 - What is the pK_a of benzoic acid if the pH of the titration was 4.46 after the addition of 25.00 mL of the base?



42. Use the portion of the titration curve for the titration of 50.00 mL of a weak acid with 0.122 M NaOH shown above left to determine the concentration and pK_a of the weak acid.
43. Use the portion of the titration curve for the titration of 20.00 mL of a weak base with 0.143 M HCl shown above right to determine the concentration and pK_b of the weak base.

COMPOSITION FROM pH

44. What are the concentrations of $C_6H_8O_6$, $C_6H_7O_6^{1-}$, and $C_6H_6O_6^{2-}$ in a solution prepared by adjusting a 0.065 M ascorbic acid solution to the following pH's?
- a) 3.0 b) 5.0 c) 10.0 d) 12.0
45. What are the concentrations of hydrosulfuric acid and the hydrogen sulfate ion in a solution prepared by adjusting a 0.10 M H_2S acid solution to the following pH's?
- a) 5.0 b) 7.0 c) 10.0 d) 13.0
46. To what pH must a 0.15 M ascorbic acid solution be adjusted to obtain the following concentrations?
- a) $[C_6H_6O_6^{2-}] = 0.040$ M
 b) $[C_6H_7O_6^{1-}] = 0.15$ M
 c) $[C_6H_6O_6^{2-}] = 2.2 \times 10^{-10}$ M
47. To what pH must a 0.10 M H_2S solution be adjusted to obtain the following sulfide ion concentrations?
- a) $[S^{2-}] = 0.085$ M
 b) $[S^{2-}] = 1.0 \times 10^{-14}$ M
 c) $[HS^{1-}] = 0.10$ M
48. NaOH is added to a 0.120 M phosphoric acid solution until the hydrogen phosphate ion concentration is 0.080 M, but the phosphate ion concentration is negligible. What is the pH of the solution?
49. HCl is added to a 0.140 M phosphate ion solution until the dihydrogen phosphate ion concentration is 0.075 M, but the hydrogen phosphate ion concentration is negligible. What is the pH?

MISCELLANEOUS PROBLEMS

50. A tablet of aspirin ($HC_9H_7O_4$) is required to contain 325 mg of aspirin. The quality is analyzed by dissolving one tablet in 50 ml H_2O , then titrating the solution with 0.1000 M NaOH. If 16.05 ml of the NaOH solution are required to reach the endpoint, how many mg of aspirin are actually in the tested sample tablet? Does this product pass your inspection?
51. In molecular biology, phosphate buffers are normally utilized to maintain a physiological pH of 6.8 to 7.4. However for RNA isolation more acidic conditions (pH around 5.8) are often required for optimal enzymatic function.
- a) Explain why an acetate buffer is preferred over a phosphate buffer for RNA isolation.
 b) How many grams of sodium acetate should be dissolved in 500. mL of 0.112 M acetic acid to prepare a pH = 5.8 buffer?
52. Recall from Chapter 2, that the colligative concentration is extremely important in a cell. Thus, both the pH and the concentration of all components are important considerations when preparing a buffer. The concentration of all particles in solution is often termed the *osmolality* or (moles of particles)·kg solvent⁻¹. Using NaH_2PO_4 and Na_2HPO_4 and water, describe how to prepare a buffer with a pH = 7.21 and an osmolality of 300. mmol·kg⁻¹.