

Chapter 7 – Mixtures of Acids and Bases

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.

7.1 The Common-Ion Effect

Introduction

Predicting the effect on an equilibrium mixture caused by the presence of an ion that appears in the equilibrium but is introduced from a separate source is something we will need to do frequently. Qualitative predictions of this type are frequently made with the use of the common ion effect, the topic of this section.

Objectives

- Explain the common-ion effect and predict the effect of a common ion on an equilibrium mixture.

7.1-1. Definition

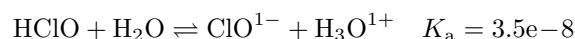
When solutions are prepared in such a way that there are two or more separate sources of an ion in an equilibrium, then that ion is referred to as a *common ion*. In this and the following chapters, we will have the occasion to deal with the effect on an equilibrium mixture caused by the addition of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

- **Common Ion Effect:** The addition of a common ion to an equilibrium mixture shifts the equilibrium away from the side of the common ion.

Thus, the concentrations of those substances on the same side of the common ion decrease while those on the opposite side increase.

7.1-2. Mixture of a Weak Acid and a Strong Acid

We examine the effect that the presence of a strong acid has on the dissociation of a weak acid by considering the dissociation of 0.10 *M* HClO in water and then in a 0.05 *M* solution of a strong acid.



We use Equation 6.6 to determine that $[\text{ClO}^{1-}] = \{(0.10)(3.5\text{e}-8)\}^{1/2} = 5.9\text{e}-5$ *M*, which is a measure of the extent of the dissociation of HClO in water. We now consider the dissociation of HClO in 0.05 *M* HCl. H_3O^{1+} is a common ion because it appears in the HClO equilibrium, but it has a separate source, the HCl. The common ion effect predicts that the presence of the common ion would reduce the concentrations of those substances on the same side of the equilibrium, so $[\text{ClO}^{1-}]$ should drop, while it increases the concentrations of those substances on the opposite side, so $[\text{HClO}]$ should increase. The solution is 0.10 *M* in HClO and 0.05 *M* in H_3O^{1+} initially, so the reaction table takes the following form:

	HClO	+	H₂O	⇌	ClO¹⁻	+	H₃O¹⁺
initial	0.10				0		0.05
Δ	- <i>x</i>				+ <i>x</i>		+ <i>x</i>
equilibrium	0.10 - <i>x</i>				<i>x</i>		0.05 + <i>x</i>

The equilibrium constant expression is

$$K_a = \frac{[\text{ClO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HClO}]} = \frac{x(0.05 + x)}{(0.10 - x)}$$

$[\text{ClO}^{1-}]$ was $5.9\text{e-}5$ M in water, and it will be less than that in the presence of acid, so we can assume that x is negligible in both the addition and the subtraction, and the equilibrium constant expression can be written as follows.

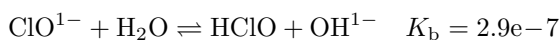
$$3.5\text{e-}8 = \frac{x(0.05)}{(0.10)}$$

Solving the above leads to $x = [\text{ClO}^{1-}] = 7.0\text{e-}8$ M , which is almost 1000 times less than in pure water. Furthermore, $[\text{H}_3\text{O}^{1+}] = 0.05 + x = 0.05$ M , i.e., the hydronium ion concentration in a solution of a strong acid and a weak acid equals the concentration of the strong acid. We conclude the following.

The presence of a strong acid suppresses the dissociation of a weak acid to the point where the strong acid is essentially the sole source of hydronium ions.

7.1-3. Mixture of a Weak Base and a Strong Base

We examine the effect that the presence of a strong base has on the dissociation of a weak base by determining the concentration of HClO in 0.10 M KClO that has been dissolved in water and then in a 0.05 M solution of a strong base.



We use Equation 6.9 to determine that $[\text{HClO}] = \{(0.10)(2.9\text{e-}7)\}^{1/2} = 1.7\text{e-}4$ M , which is a measure of the extent of the reaction in water. We now look at the reaction in 0.05 M NaOH . The common ion effect predicts that the presence of additional OH^{1-} , the common ion, will reduce $[\text{HClO}]$ and increase $[\text{ClO}^{1-}]$. The solution is 0.10 M in ClO^{1-} and 0.05 M in OH^{1-} initially, so the reaction table takes the following form.

	ClO^{1-}	+	H_2O	\rightleftharpoons	HClO	+	OH^{1-}
initial	0.10				0		0.05
Δ	$-x$				$+x$		$+x$
equilibrium	$0.10 - x$				x		$0.05 + x$

The equilibrium constant expression is

$$K_b = \frac{[\text{HClO}][\text{OH}^{1-}]}{[\text{ClO}^{1-}]} = \frac{x(0.05 + x)}{(0.10 - x)}$$

$[\text{HClO}]$ was $1.7\text{e-}4$ M in water, and it will be less than that in the presence of base, so we can assume that x is negligible in both the addition and the subtraction. The equilibrium constant expression is then the following.

$$2.9\text{e-}7 = \frac{x(0.05)}{(0.10)}$$

Solving the above leads to $x = [\text{HClO}] = 5.8\text{e-}7$ M , which is almost 1000 times less than in pure water. Furthermore $[\text{OH}^{1-}] = 0.05 + x = 0.05$ M , i.e., the hydroxide ion concentration in a solution of a strong base and a weak base equals the concentration of the strong base. We conclude the following.

The presence of a strong base suppresses the dissociation of a weak base to the point where the strong base is essentially the sole source of hydroxide ions.

7.2 Buffers

Introduction

In Chapter 6, we discussed four types of acid-base solutions in some detail: strong acid, strong base, weak acid, and weak base. We now discuss 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 pH change resulting from the addition of a strong acid or base. 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. In this section, we discuss the action of buffers.

Objectives

- Define a buffer and explain how it works.
- Choose an appropriate conjugate acid-base pair to use in the preparation of a buffer of a known pH.
- Determine the base to acid ratio required to produce a buffer of given pH.
- Determine the pH of a buffer given the amounts of acid and base present.
- Calculate the change in pH expected when a strong acid or base is added to a buffered solution.

7.2-1. Introduction to Buffers Video

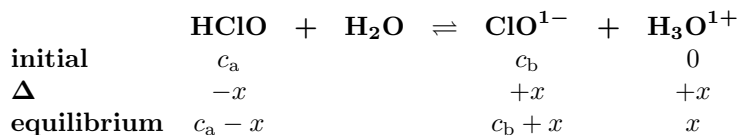
A video or simulation is available online.

7.2-2. Definition

A *buffer* is a solution of a weak acid and its conjugate base in *comparable* and *appreciable* amounts. They 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 to much weaker acids and bases by the action of the buffer.

7.2-3. Hydronium Ion Concentrations in Buffer Solutions

A buffer contains both the weak acid and the 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, because pH is more common than pOH, we use the acid dissociation reaction to discuss buffered solutions because it contains the hydronium ion directly. Consider a hypochlorous acid/hypochlorite ion buffer in which the initial concentrations of the acid (c_a) and the base (c_b) are comparable. The reaction table for the acid dissociation of acid in the presence of the base has the following form:



The equilibrium constant expression for the reaction is:

$$K_a = \frac{[\text{ClO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HClO}]} = \frac{(c_b + x)x}{(c_a - x)}$$

The presence of the conjugate base suppresses the dissociation of the acid, so x is negligible in both the addition and the subtraction. Consequently, the equilibrium constant expression can be written as the following:

$$K_a = \frac{c_b x}{c_a}$$

Solving for the above for hydronium ion concentration (x), we obtain Equation 7.1.

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

Hydronium ion Concentration in a Buffer Solution (7.1)

$c_a = n_a/V$ and $c_b = n_b/V$, and the volumes cancel in the ratio c_a/c_b . Thus, $c_a/c_b = n_a/n_b$, i.e., the ratio of the concentrations equals the ratio of the numbers of moles.

Taking the negative logarithms of both sides of Equation 7.1 we obtain the equation that is known as the Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_{\text{a}} + \log\left(\frac{c_{\text{b}}}{c_{\text{a}}}\right) = \text{p}K_{\text{a}} + \log\left(\frac{n_{\text{b}}}{n_{\text{a}}}\right)$$

Henderson-Hasselbalch Equation (7.2)

where the identity $\log(x/y) = -\log(y/x)$ has been used. Equation 7.2 is the most common method for determining the pH of a buffer.

7.2-4. Buffer pH Exercise

EXERCISE 7.1:

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

(Refer to the Acid-Base Table with $\text{p}K_{\text{a}}$ and Equation 7.2.)

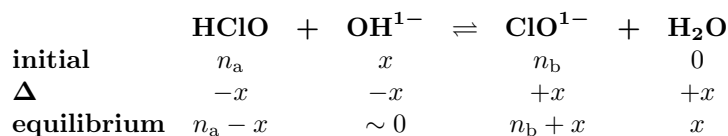
$\text{p}K_{\text{a}} =$ _____ $c_{\text{a}} =$ _____ *M*
 $c_{\text{b}} =$ _____ *M* $\text{pH} =$ _____

7.2-5. Buffer Action Video

A video or simulation is available online.

7.2-6. Buffer Action Against Addition of Base

Buffers act to protect the solution from drastic pH changes resulting from the addition of hydronium or hydroxide ions. They do so by reacting with the added acid or base. However, **in order for the buffer to function properly, it must be the excess reactant.** Consider the case where x mmol OH^{1-} ion are added to a buffer solution that contains n_{a} mmol HClO and n_{b} mmol ClO^{1-} . The strong base reacts extensively with the weak acid in the buffer, so, as long as HClO is in excess, all of the hydroxide reacts. The reaction table has the following form:



Of course $[\text{OH}^{1-}]$ cannot be zero, which is why the approximate sign is used, but it will be very small compared to the weak base concentration. The above reaction table is valid, and the solution is a buffer only so long as there is sufficient acid to react with the base. In other words, an **appreciable amount of acid is required.** The resulting solution is a solution of a weak acid and its conjugate base, so it is still a buffer solution, and Equation 7.2 can still be used to determine its pH.

7.2-7. Strong Base–Buffer Worked Example

A video or simulation is available online.

7.2-8. Buffer Action with Strong Base Exercise

EXERCISE 7.2:

In a previous exercise, we determined that the pH of a buffer that is 0.600 *M* potassium acetate and 0.750 *M* acetic acid is 4.64.

What is the pH of a solution prepared by adding 10. mL of 6.0 *M* NaOH to 200. mL of this buffer?

First, complete the reaction table for the reaction of the weak acid with the strong base. Note that all entries are in mmol. (Refer to the Acid-Base Table with pK_a and Equation 7.2.)

	Reacting Acid	+	Reacting Base	→	Produced Base	+	Produced Acid
		+		→		+	
initial							mmol
Δ							mmol
equilibrium							mmol
pH = _____							

7.2-9. Buffer Action Against Addition of Acid

Consider the case where x mmol of H_3O^{1+} ions are added to a buffer solution that contains n_a mmol HClO and n_b mmol ClO^{1-} . The strong acid reacts extensively with the weak base in the buffer, so, as long as ClO^{1-} is in excess, all of the hydronium reacts. The reaction table has the following form:

	ClO^{1-}	+	H_3O^{1+}	\rightleftharpoons	HClO	+	H_2O
initial	n_b		x		n_a		0
Δ	$-x$				$+x$		$+x$
equilibrium	$n_b - x$		~ 0		$n_a + x$		x

$[\text{H}_3\text{O}^{1+}]$ cannot be zero, which is why the approximate sign is used, but it will be very small compared to the weak acid concentration. The above reaction table is valid, and the solution is a buffer only so long as there is sufficient base to react with the acid. In other words, **an appreciable amount of base is required**. The resulting solution is a solution of a weak acid and its conjugate base, so it is still a buffer solution, and Equation 7.2 can still be used to determine its pH.

7.2-10. Buffer Action with Strong Acid Exercise

EXERCISE 7.3:

What is the pH of a solution prepared by adding 10. mL of 6.0 M HCl to 200. mL of the buffer?

Complete the reaction table for the reaction of the weak base with the strong acid in millimoles. (Refer to the Acid-Base Table with pK_a and Equation 7.2.)

	Reacting Base	+	Reacting Acid	→	Produced Acid	+	Produced Base	
		+		→		+		
initial								mmol
Δ								mmol
equilibrium								mmol

pH = _____

7.2-11. Buffer Exercise

EXERCISE 7.4:

A buffer is 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 .

(a) What is the pH of the buffer?

$n_a =$ _____ mol

$pK_a =$ _____

$n_b =$ _____ mol

pH = _____

(b) What would be the pH of the buffer solution after the addition of 22.8 mL of 1.45 M NaOH?

	Reacting Acid	+	Reacting Base	→	Produced Base	+	Produced Acid	
		+		→		+		
initial								mol
Δ								mol
equilibrium								mol

Use Equation 7.2 to determine the pH.

pH = _____

7-2.12. Buffer Capacity

There must be appreciable amounts of the acid and its conjugate base in a buffer to assure that it has acceptable *buffer capacity*, which is the amount of acid or base that can be added without destroying the effectiveness of the buffer. Thus, a buffer solution has a large buffer capacity if it contains a large number of moles of the weak acid and of the weak base.

7.2-13. Buffer Range

A buffer functions well 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 of an acetic acid/acetate ion buffer and the mole fractions of the acid and the base. The buffer range is the pH range over which the mole fractions change most dramatically with pH (highlighted by the box in the figure).

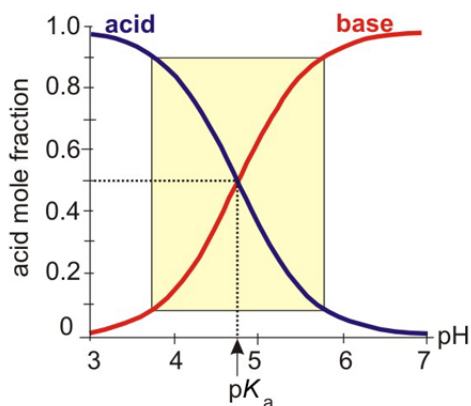


Figure 7.1: Effective Buffer Range The mole fractions of acetic acid and its conjugate base as a function of pH. The effective buffer range is indicated by the box. The pH of a buffer solution in which the two mole fractions are equal is equal to the pK_a of the acid.

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 and $\log 1 = 0$ to the midpoint indicates that $\text{pH} = pK_a$. Thus, buffers are most effective at pH values near their pK_a .

As shown in Figure 7.1, buffers operate acceptably in the range where the mole fraction of the acid or base is in the range of 0.1 to 0.9, which means that $0.1 < c_a/c_b < 10$.

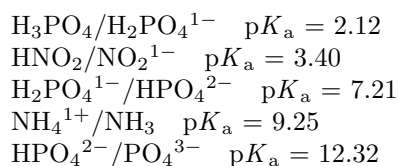
We conclude that a buffer is effective at a pH that is within one pH unit of its pK_a .

7.2-14. Preparing a pH = 7 Buffer Exercise

EXERCISE 7.5:

How would you prepare a pH = 7.00 buffer?

First, select the best buffer system for this pH.



Next, use Equation 7.2 to determine $\log(n_b/n_a)$.

$$\log(n_b/n_a) = \underline{\hspace{2cm}}$$

Take the antilog to obtain the ratio.

$$n_b/n_a = \underline{\hspace{2cm}}$$

Assume you have 1.50 L of a 0.840 *M* solution of the acid and determine the number of moles of base that would have to be added to produce the buffer.

moles of acid present = _____ mol

moles of base present = _____ mol

7.2-15. Preparing a pH = 9.8 Buffer Exercise

EXERCISE 7.6:

How many moles of base should be added to 500. mL of 0.222 *M* acid to prepare a pH = 9.80 buffer solution?

First, select the best buffer system for this pH.

$\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^{1-}$ $pK_a = 2.12$

$\text{HNO}_2/\text{NO}_2^{1-}$ $pK_a = 3.40$

$\text{H}_2\text{PO}_4^{1-}/\text{HPO}_4^{2-}$ $pK_a = 7.21$

$\text{NH}_4^{1+}/\text{NH}_3$ $pK_a = 9.25$

$\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ $pK_a = 12.32$

Next, use Equation 7.2 to determine $\log(n_b/n_a)$.

$\log(n_b/n_a) = \text{_____}$

Take the antilog to obtain the ratio.

$n_b/n_a = \text{_____}$

Determine the number of moles of base that would have to be added to the acid.

moles of acid = _____ mol

moles of base = _____ mol

7.3 Acid-Base Composition from Reactant Amounts

Introduction

We have now treated five different types of acid-base solutions and shown how to determine $[\text{H}_3\text{O}^{1+}]$, $[\text{OH}^{1-}]$, and pH of each:

- 1 Strong acid:** Strong acids dissociate completely, so $[\text{H}_3\text{O}^{1+}] = c_o$.
- 2 Strong base:** Strong bases ($\text{M}(\text{OH})_n$) dissociate completely, so $[\text{OH}^{1-}] = nc_o$.
- 3 Weak acid:** Solve the K_a expression for $[\text{H}_3\text{O}^{1+}]$ using Equation 6.6.
- 4 Weak base:** Solve the K_b expression for $[\text{OH}^{1-}]$ using Equation 6.9.
- 5 Buffers:** Solve the K_a expression for $[\text{H}_3\text{O}^{1+}]$ using Equation 7.1 or solve directly for pH using Equation 7.2.

Thus, there are four types of acid-base reactions. (When buffers react, they do so as the weak acid or the weak base.)

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

In this section, we examine acid-base properties of the solutions that result from these reactions.

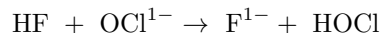
Objectives

- Write acid-base reactions and determine their equilibrium constants from the K_a 's of the reacting and produced acids.
- 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).

Weak Acid–Weak Base Reactions

7.3-1. The Equilibrium Constant

Consider the following reaction.



The equilibrium constant expression for the reaction is

$$K = \frac{[\text{F}^{1-}][\text{HOCl}]}{[\text{HF}][\text{OCl}^{1-}]}$$

Compare that with the expression obtained by dividing the K_a expression of the reacting acid (HF) by that of the produced acid (HOCl).

$$\frac{K_a(\text{HF})}{K_a(\text{HOCl})} = \frac{[\text{H}_3\text{O}^{1+}][\text{F}^{1-}]}{[\text{HF}]} \times \frac{[\text{HOCl}]}{[\text{H}_3\text{O}^{1+}][\text{OCl}^{1-}]} = \frac{[\text{F}^{1-}][\text{HOCl}]}{[\text{HF}][\text{OCl}^{1-}]}$$

Note that the hydronium ion concentrations cancel to produce the K_a expression, which is identical to the equilibrium expression for the reaction of HF with OCl^{1-} ion. Thus, the equilibrium constant for the reaction can be determined as shown below.

$$K = \frac{K_a \text{ of reacting acid HF}}{K_a \text{ of produced acid HOCl}} = \frac{7.2\text{e-}4}{3.5\text{e-}8} = 2.1\text{e}+4$$

We conclude that the equilibrium constant for an acid-base reaction can be determined from the acid dissociation constants of the reacting and produced acids as follows.

$$K = \frac{K_a(\text{reacting acid})}{K_a(\text{produced acid})} \quad \text{Equilibrium Constant for an Acid-Base Reaction} \quad (7.3)$$

The produced acid is the conjugate acid of the reacting base. The strength of an acid is inversely proportional to the strength of its conjugate base, so the above expression indicates that the value of K depends upon the relative strengths of the reacting acid and base. If both are relatively strong, then both K_a (reacting acid) and K_b (reacting base) are large. However, if K_b (reacting base) is large, then K_a (produced acid) must be small, which makes the equilibrium constant of the reaction large.

7.3-2. Determining K Exercise

EXERCISE 7.7:

Determine the value of K for the following aqueous weak acid–weak base reactions.

Reaction	K_a (reacting acid)	K_a (produced acid)	K
$\text{HNO}_2 + \text{F}^{1-} \rightleftharpoons \text{NO}_2^{1-} + \text{HF}$			
$\text{HCN} + \text{CH}_3\text{COO}^{1-} \rightleftharpoons \text{CN}^{1-} + \text{CH}_3\text{COOH}$			
$\text{NH}_3 + \text{HSO}_4^{1-} \rightleftharpoons \text{NH}_4^{1+} + \text{SO}_4^{2-}$			

7.3-3. Mixing Exercise

EXERCISE 7.8:

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 ? Fill in the reaction table with molar concentration, and use x to indicate the final concentration of NO_2^{1-} .

Use the Acid-Base Table with $\text{p}K_a$ to determine the value of the equilibrium constant.

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

The reaction table:

	Reacting Acid	+	Reacting Base	→	Produced Base	+	Produced Acid	
		+		→		+		
initial								mol
Δ								mol
equilibrium								mol

Set up the equilibrium constant expression. It is a perfect square, so take the square root of both sides to determine the answer.

$$[\text{NO}_2^{1-}] = \underline{\hspace{2cm}} M$$

7.3-4. Overview of Extensive Reactions

The remainder of the acid-base reaction types all involve a strong acid and/or a strong base, so they are all extensive. Consequently, the limiting reactant is assumed to disappear completely, which means that there are no unknowns in the reaction table. We will use the following method in each case:

- Write the chemical equation and construct the reaction table. We will use millimoles in the reaction table because the volumes are all given in milliliters, but molarities can also be used.
- Identify the type of solution that results from the mixing based upon the equilibrium entries.
 - Strong acid if the entry under $[\text{H}_3\text{O}^{1+}]$ is not zero. There can be no base present if there is some H_3O^{1+} because they would react, and a weak acid can be ignored in the presence of a strong acid.
 - Strong base if the entry under OH^{1-} is not zero. There can be no acid present if there is some OH^{1-} because they would react, and a weak base can be ignored in the presence of a strong one.

- Weak acid if the only nonzero entry lies under a weak acid.
- Weak base if the only nonzero entry lies under a weak base.
- Buffer if the entries under both the weak acid and its conjugate base are nonzero.

3 Determine $[\text{H}_3\text{O}^{1+}]$, $[\text{OH}^{1-}]$, pH, or pOH using the equation appropriate to the solution type above.

We will apply the above method to each of the reaction types in the following sections.

7.3-5. Titration Curves

Recall from Section 2.4-5. that the equivalence point in an acid-base titration is that point where the number of moles of analyte in the initial flask equals the number of moles of titrant that are added, which is summarized as follows.

- **Equivalence Point:** moles acid = moles base, so $M_{\text{acid}} V_{\text{acid}} = M_{\text{base}} V_{\text{base}}$

The above expression was then used to determine M_{acid} from a known M_{base} and the known volumes.

We now examine the pH of the acid solution as a function of the volume of base that is added to generate the titration curve for the titration. A *titration curve* is a plot of the pH of the solution as a function of the volume of a titrant. The shape of the curve depends on the nature of both the acid and base, and we start by examining the titration of a strong acid with a strong base in the following video.

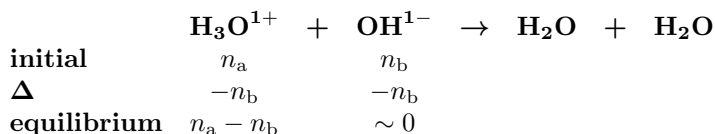
Strong Acid–Strong Base Reactions

7.3-6. Strong Acid–Strong Base Titration Video

A video or simulation is available online.

7.3-7. Method

Our first titration curve is for the titration of a strong acid with a strong base. We start out with n_a moles of acid and determine the pH after n_b moles of base have been added. The reaction is extensive, so there is essentially no limiting reactant present at equilibrium and the solution type is dictated solely by the reactant in excess. The solution type depends upon the relative values of n_a and n_b , and the following reaction table shows the case where the base is the limiting reactant:



The equilibrium solution is a strong acid that contains $n_a - n_b$ mol of acid in a total volume $V_{\text{total}} = V_{\text{acid}} + V_{\text{base}}$, so $[\text{H}_3\text{O}^{1+}] = (n_a - n_b)/V_{\text{total}}$.

At the equivalence point, $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}]$, so pH = 7.0 at 25 °C. Beyond the equivalence point, OH^{1-} is in excess and the equilibrium solution is one of a strong base. The following table summarizes these conclusions:

Moles	Solution Type	Moles of Excess Reactant	
$n_a > n_b$	strong acid	$n_a - n_b$ mol H_3O^{1+}	pH = $-\log[\text{H}_3\text{O}^{1+}]$
$n_a = n_b$	neutral	no excess reactant	pH = 7.00
$n_a < n_b$	strong base	$n_b - n_a$ mol OH^{1-}	pOH = $-\log[\text{OH}^{1-}]$

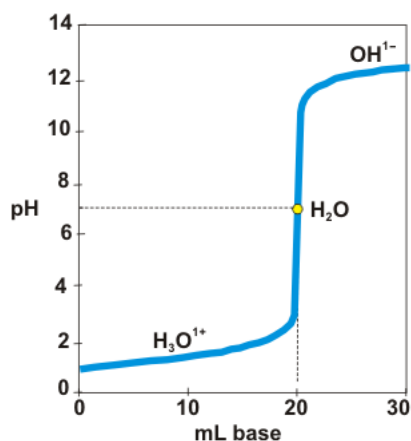
Table 7.1: Solution Types Resulting From Mixing a Strong Acid and a Strong Base

Solution type resulting from the reaction of n_a moles of a *strong acid* with n_b moles of a *strong base*.

7.3-8. SA–SB Titration Curve Exercise

EXERCISE 7.9:

A strong acid–strong base titration curve is shown below. The equivalence point (yellow circle) in a strong acid–strong base titration is pure water, so the pH is 7.00.



Determine the pH after the addition of 10.0 mL, 20.0 mL, and 30.0 mL of base in the titration of 20.0 mL of 0.100 M HCl with 0.100 M NaOH.

Put the number of millimoles of excess reactant present at equilibrium in the “xs” line or 0 if neither reactant is in excess.

	10.0 mL base	20.0 mL base	30.0 mL base	
n_a				mmol
n_b				mmol
xs				mmol
total volume				mL
xs concentration				M
pH				mmol

Weak Acid–Strong Base Reactions

7.3-9. Weak Acid–Strong Base Titration Video

A video or simulation is available online.

7.3-10. Weak Acid–Strong Base Titration Calculations

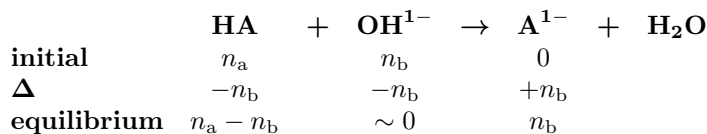
We now examine the titration curve for the titration of n_a moles of a weak acid HA with hydroxide ion.

Initially the solution is one of the weak acid HA, so if less than 5% of the acid reacts, we can write

$$[\text{H}_3\text{O}^{1+}] = (cK_a)^{1/2}$$

where c is the concentration of HA.

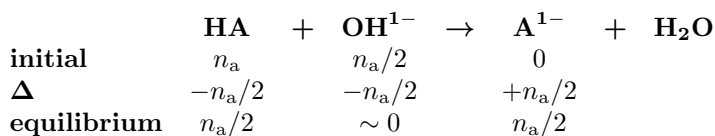
OH¹⁻ is limiting reactant. The reaction table has the following form:



The equilibrium line contains both a weak acid and its conjugate base, so it is a buffer solution, and we can use the Henderson-Hasselbalch equation to determine the pH.

$$\text{pH} = \text{p}K_a + \log \frac{n_b}{n_a - n_b}$$

A special case in this region occurs at the **midpoint of the titration**; i.e., when $n_b = n_a/2$. In this special case the table would be

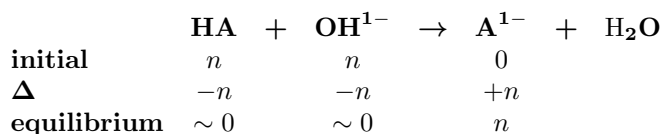


Thus, the resulting solution is still a buffer, but at the midpoint of the titration the number of moles of HA and A¹⁻ are equal. The ratio $(n_b/n_a) = 1$ and $\log(1) = 0$, so the Henderson-Hasselbalch equation becomes,

$$\text{pH} = \text{p}K_a + \log(1) = \text{p}K_a$$

The pH at the midpoint of a titration of a weak acid with a strong base is equal to the pK_a of the acid.

At the **equivalence point**, $n_a = n_b = n$, so the reaction table would be



The only equilibrium entry that is not zero is under the weak base, so the solution is a weak base solution that contains n mol of the weak base. The [OH¹⁻] of this weak acid solution would be determined as follows:

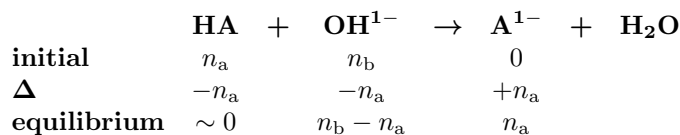
$$[\text{A}^{1-}] = c_b = n/V_{\text{total}}$$

$$K_b = 1.0\text{e-}14/K_a$$

$$[\text{OH}^{1-}] = (c_b K_b)^{1/2}$$

Note that in the titration of a weak acid with a strong base, the solution at the equivalence point is that of a weak base, so $\text{pH} > 7$.

When **HA is the limiting reactant**, the reaction table is given as the following:



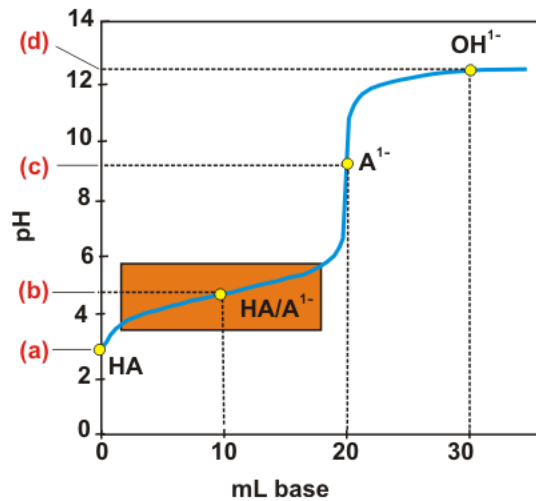
The equilibrium entry under OH¹⁻ is not zero, so the solution is a strong base that contains $n_b - n_a$ mol of base. The presence of the weak base does not impact the pH of the solution due to the common ion effect, so we can write

$$[\text{OH}^{1-}] = \frac{n_b - n_a}{V_{\text{total}}}$$

7.3-11. WA–SB Titration Curve Exercise

EXERCISE 7.10:

Determine the pH at **points (a)–(d)** in the titration curve of 20.0 mL of 0.100 M HC₂H₃O₂ with 0.100 M NaOH shown below. The orange rectangle outlines the buffer region.



$n_a =$ _____ mmol acid initially

point (a) 0 mL ($n_b = 0$ – weak acid)

$[H_3O^{1+}] =$ _____ M pH = _____

point (b) 10.0 mL ($0 < n_b < n_a$: buffer)

$n_b =$ _____ mmol base added weak base produced = _____ mmol
 weak acid remaining = _____ mmol pH = _____

point (c) 20.0 mL ($n_b = n_a$: equivalence point, weak base)

$n_b =$ _____ mmol base added $[CH_3COO^{1-}] =$ _____ M
 weak acid remaining = _____ mmol $[OH^{1-}] =$ _____ M
 weak base produced = _____ mmol pH = _____

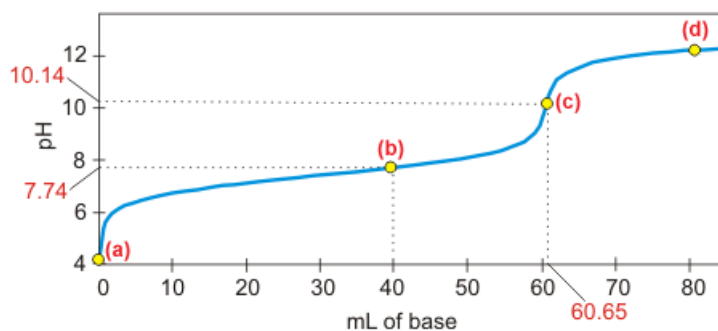
point (d) 30.0 mL ($n_b > n_a$: strong base)

$n_b =$ _____ mmol base added $[OH^{1-}] =$ _____ M
 excess $OH^{1-} =$ _____ mmol pH = _____

7.3-12. Using a Titration Curve Exercise

EXERCISE 7.11:

Consider the titration curve for the titration of 50.00 mL of an unknown weak acid with 0.122 M NaOH that is shown below.



Determine the concentration of the weak acid and its pK_a .

volume of base at the equivalence point: _____ mL

mmol base added at equivalence point: _____ mmol

mmol acid present initially: _____ mmol

concentration of original acid: _____

The solution type at **point (b)** is which of the following?

- weak acid
- strong base
- weak base
- buffer

mmol of hydroxide added at **point (b)** = _____ mmol

equilibrium mmol weak acid at **point (b)** = _____ mmol

equilibrium mmol conjugate base at **point (b)** = _____ mmol

pK_a = _____

7.3-13. The Shape of an Acid-Strong Base Titration Curve

The general shape of a titration curve consists of a sharp rise in pH in the vicinity of the equivalence point, but how steep the slope of the rise is depends upon the strength of the acid. Compare the titration curves for the titrations of 0.1 M HCl, 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$, and 0.1 M HCN. In each case, the final pH approaches the pH of the strong base, which would be 13.0 in the case of 0.1 M NaOH. However, the pH at the midpoint of the titration varies with the acid strength. Thus, the pH is about 1.5 at the midpoint in the titration of 0.10 M HCl, but it equals the pK_a of the acid for a weak acid, which is 4.74 for $\text{HC}_2\text{H}_3\text{O}_2$ and 9.40 for HCN. Thus, the rise of the curve in the case of a strong acid is about 12 pH units, but it is only about 8 pH units for $\text{HC}_2\text{H}_3\text{O}_2$ and about 3 pH units for HCN. The less dramatic change in pH associated with very weak acids can make it difficult to get as a precise determination of the equivalence point.

7.3-14. Mixing Exercise

EXERCISE 7.12:

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 KHSO₄?

The reaction table:

	HSO₄¹⁻	+	OH¹⁻	⇌	SO₄²⁻	+	H₂O	
initial								mmol
Δ								mmol
equilibrium								mmol

The resulting solution type is which of the following?

- weak acid
- strong base
- weak base
- buffer

[SO₄²⁻] = _____ M

[OH¹⁻] = _____ M

K_b = _____

pH = _____

7.3-15. Polyprotic Acid–Strong Base Titration Video

A video or simulation is available online.

7.3-16. Polyprotic Acid–Strong Base

Polyprotic acids dissociate one proton at a time, and they are deprotonated by OH¹⁻ 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. Consider the titration of H₂A with a strong base. The following reaction table covers the reaction up to the first equivalence point.

	H₂A	+	OH¹⁻	→	HA¹⁻	+	H₂O	
initial	<i>n_a</i>		<i>n_b</i>		0			mmol
Δ	- <i>n_b</i>		- <i>n_b</i>		+ <i>n_b</i>			mmol
equilibrium	<i>n_a - n_b</i>		~ 0		+ <i>n_b</i>			mmol

Thus, adding hydroxide to H₂A produces a solution that can be treated as an H₂A/HA¹⁻ buffer. At the first equivalence point, the solution is that of an amphiprotic substance, so we can use Equation 6.13, which is shown below, to determine its pH.

$$\text{pH} = 1/2(\text{p}K_1 + \text{p}K_2)$$

The following reaction table then covers the reaction between the first and second equivalence points. Note that the first titration creates *n_a* mmol of HA¹⁻, so we use that for the initial amount of weak acid. *n_b* is the number of mmoles of base added after the first equivalence point.

	HA¹⁻	+	OH¹⁻	→	A²⁻	+	H₂O	
initial	<i>n_a</i>		<i>n_b</i>		0			mmol
Δ	- <i>n_b</i>		- <i>n_b</i>		+ <i>n_b</i>			mmol
equilibrium	<i>n_a - n_b</i>		~ 0		+ <i>n_b</i>			mmol

Adding hydroxide to HA^{1-} produces a solution that can be treated as an $\text{HA}^{1-}/\text{A}^{2-}$ buffer. At the second equivalence point, the solution is that of the weak base A^{2-} . After the second equivalence point the solution is a strong base. The resulting titration curve is shown in Figure 7.2.

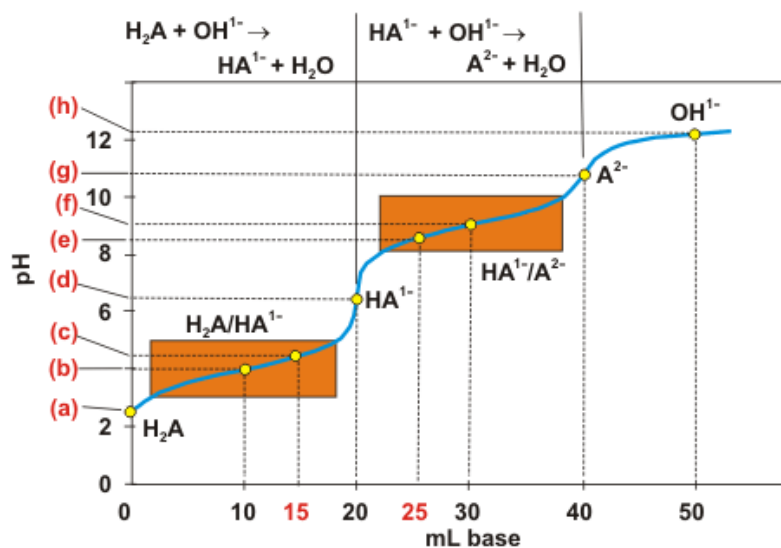


Figure 7.2: Diprotic acid–Strong base Titration Curve The rectangles outline the two buffer ranges. The points on the graph represent the following: (a) weak acid H_2A ; (b) 1st midpoint so $\text{pH} = \text{p}K_1$; (c) $\text{H}_2\text{A}/\text{HA}^{1-}$ buffer; (d) 1st equivalence point, amphoteric HA^{1-} ; (e) $\text{HA}^{1-}/\text{A}^{2-}$ buffer; (f) 2nd midpoint so $\text{pH} = \text{p}K_2$; (g) 2nd equivalence point, weak base A^{2-} ; and (h) strong base solution.

7.3-17. Polyprotic Titration Curve Exercise

EXERCISE 7.13:

Determine the pH at various points in the titration curve for the titration of 20.0 mL of 0.100 M H₂A (pK₁ = 4.00, pK₂ = 9.00) with 0.100 M NaOH. The titration curve is shown in Figure 7.2. You should construct a reaction table at each point, determine the solution type, and then the pH.

$$n_a = \text{_____ mmol}$$

point (b) 10.0 mL (midway to first equivalence point)

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

point (c) 15.0 mL (buffer region of first equivalence point)

$$n_b = \text{_____ mmol}$$

$$\text{eq mmol H}_2\text{A} = \text{_____ mmol}$$

$$\text{eq mmol HA}^{1-} = \text{_____ mmol}$$

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

point (d) 20.0 mL (solution of amphiprotic substance HA¹⁻)

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

point (e) 25.0 mL (buffer region of second equivalence point)

$$n_b = \text{_____ mmol from first eq point}$$

$$\text{eq mmol HA}^{1-} = \text{_____ mmol}$$

$$\text{eq mmol A}^{2-} = \text{_____ mmol}$$

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

point (f) 30.0 mL (midway to second equivalence point)

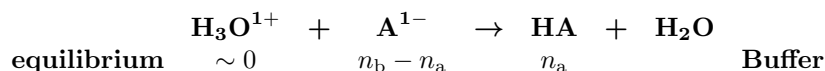
$$\text{pH} = \text{_____}$$

Strong Acid–Weak Base Reactions

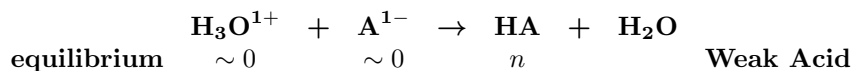
7.3-18. Summary of Strong Acid–Weak Base Reactions

The reaction between a strong acid and a weak base is treated analogously with that between a weak acid and a strong base. The nature of the resulting solution depends upon the relative number of moles of acid (n_a) and base (n_b).

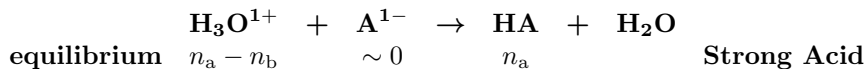
$n_a < n_b$: acid is limiting reactant



$n_a = n_b = n$: acid and base in stoichiometric amounts



$n_a > n_b$: base is limiting reactant



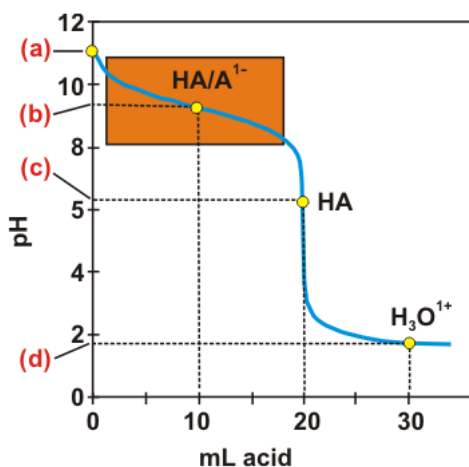
7.3-19. Strong Acid–Weak Base Titration

A video or simulation is available online.

7.3-20. Strong Acid–Weak Base Titration Curve

EXERCISE 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.



- (a) $n_a = 0$: a solution of the weak base NH_3 .
- (b) $n_a < n_b$: a buffer solution. $\text{pH} = \text{p}K_a$ at **point (b)**.
- (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.

initial mmoles of weak base, $n_b =$ _____ mmol

point (a) 0.0 mL (weak base) pH = _____

point (b) 10.0 mL (buffer) pH = _____

point (c) 20.0 mL (equivalence point, weak acid) pH = _____

point (d) 30.0 mL (strong acid) pH = _____

Making Buffers by Reaction

7.3-21. Three Ways to Make Buffers

We have now seen three ways in which buffers can be made:

- 1 mixing the acid and its conjugate base directly in the appropriate ratio to achieve the required pH
- 2 adding a strong acid to an excess of weak base until the required pH is achieved
- 3 adding a strong base to an excess of weak acid until the required pH is achieved

Examples of the first method were presented in CAQS Section 7.2, and an example of the second method is presented in the following section.

7.3-22. Preparing a Buffer with a Strong Acid and a Weak Base

EXERCISE 7.15:

How many mL of 0.26 M HCl must be added to 500. mL of 0.12 M NH₃ to make a pH = 10.00 buffer?

First, construct the reaction table using x for the number of mmols of H₃O¹⁺ that are required.

Answer the following questions about the pH = 10.00 solution to obtain the volume of acid that would be needed.

pK_a (Acid-Base Table with pK_a) _____

mmol NH₃ in initial solution _____

$\log\left(\frac{\text{mmol NH}_3}{\text{mmol NH}_4^{1+}}\right)$ _____

$\frac{\text{mmol NH}_3}{\text{mmol NH}_4^{1+}}$ _____

mmol NH₄¹⁺ (in terms of x) in equilibrium mixture _____

mmol NH₃ (in terms of x) in equilibrium mixture _____

Use the ratio and mmols to solve for x . _____ mmol H₃O¹⁺

volume of 0.26 M HCl required _____ mL

7.4 Acid-Base Composition from Equilibrium pH

Introduction

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? We answer that question in this section.

7.4-1. Method

One equation is required for each unknown concentration in a solution, so determining [H₂X], [HX¹⁻], and [X²⁻] 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, which is based on the fact that even though reaction may take place in solution, the total amount of X does not change; i.e., $c_o = [\text{H}_2\text{X}] + [\text{HX}^{1-}] + [\text{X}^{2-}]$. Fortunately, chemistry can often 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 values, 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, so

- the acid concentration is negligible if $[\text{base}]/[\text{acid}] > 100$, and
- the base concentration is negligible if $[\text{base}]/[\text{acid}] < 0.01$

We use the above conditions in the Henderson-Hasselbalch equation to conclude the following.

- the acid is negligible if $\text{pH} > \text{p}K_a + \log(100) = \text{p}K_a + 2$
- the base is negligible if $\text{pH} < \text{p}K_a + \log(0.01) = \text{p}K_a - 2$

The concentration of an acid and its conjugate base are both appreciable at pH's within 2 pH units of the $\text{p}K_a$ of the acid, but only the acid can be appreciable below this pH range, and only the base can be appreciable above it.

7.4-2. Concentrations vs. pH

Monoprotic Acid: The concentrations of CH_3COOH and $\text{CH}_3\text{COO}^{1-}$ as a function of pH are shown in Figure 7.3. The $\text{p}K_a$ of CH_3COOH is 4.7, so $[\text{CH}_3\text{COOH}] = c_o$ if $\text{pH} < 2.7$ ($\text{pH} = 4.7 - 2$), but $[\text{CH}_3\text{COO}^{1-}] = c_o$ if $\text{pH} > 6.7$ ($4.7 + 2$). At intermediate pH values ($2.7 < \text{pH} < 6.7$), neither concentration is negligible, so we use $[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^{1-}] = c_o$. Thus, the solution is treated as a buffer in the yellow region of the figure, as an acetic acid solution at lower pH, and as an acetate ion solution at higher pH.

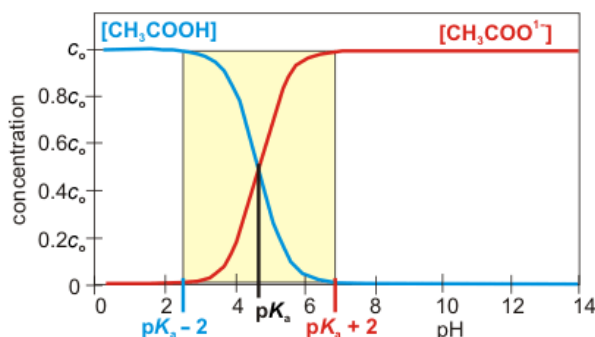


Figure 7.3: Concentrations of acetic acid and acetate ion as a function of pH. The $[\text{acid}] \sim c_o$ and $[\text{base}] \sim 0$ at pH's below $(\text{p}K_a - 2)$, but $[\text{acid}] \sim 0$ and $[\text{base}] \sim c_o$ at pH's above $(\text{p}K_a + 2)$. The concentrations of both substances are appreciable only in the yellow region. $\text{p}K_a = 4.74$

Diprotic Acid: The case of the diprotic acid H_2S ($\text{p}K_1 = 7.0$, $\text{p}K_2 = 12.9$) is shown in Figure 7.4. The two yellow boxes represent the two pH ranges ($\text{p}K_a \pm 2$) 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 values of pH.

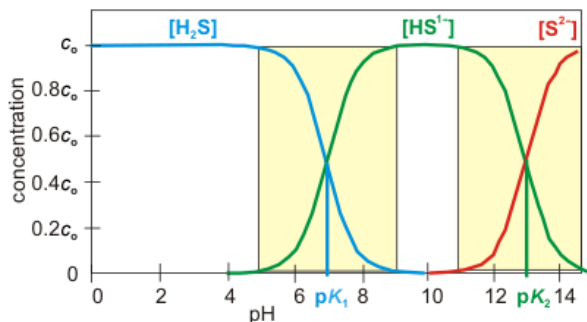


Figure 7.4: Concentrations of hydrosulfuric acid, hydrogen sulfide ion, and sulfide ion as a function of pH. The concentrations of two substances are comparable and appreciable in the yellow boxes, but only one component is appreciable outside. The pH ranges of the yellow boxes are from $\text{pH} = \text{p}K_a - 2$ to $\text{pH} = \text{p}K_a + 2$.

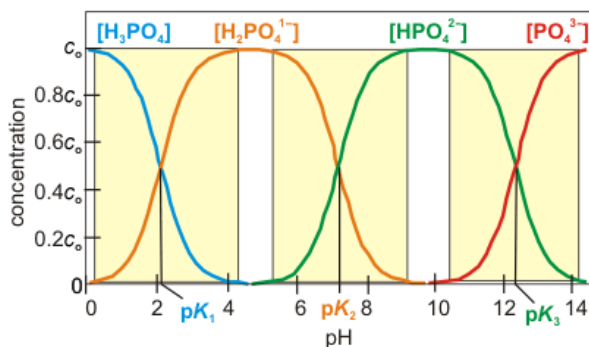
Triprotic Acid: The example of a triprotic acid, H_3PO_4 , is considered in the following exercise. Even though there are four concentrations to determine, no more than two are appreciable at any pH.

7.4-3. Triprotic Exercise

EXERCISE 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. Use the Acid-Base Table with pK_a to get the pK_a 's.

$pK_1 =$ $pK_2 =$ $pK_3 =$



pH = 7.00

The number of appreciable concentrations is _____

$[\text{H}_2\text{PO}_4^{1-}] =$ _____ M $[\text{H}_3\text{PO}_4] =$ _____ M

$[\text{HPO}_4^{2-}] =$ _____ M $[\text{PO}_4^{3-}] =$ _____ M

pH = 10.00

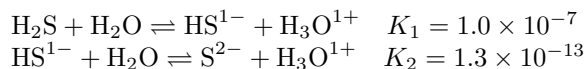
The number of appreciable concentrations is _____

$[\text{HPO}_4^{1-}] =$ _____ M $[\text{H}_2\text{PO}_4^{1-}] =$ _____ M

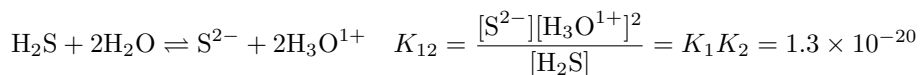
$[\text{PO}_4^{3-}] =$ _____ M $[\text{H}_3\text{PO}_4] =$ _____ M

7.4-4. Combining Equilibria

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



Adding the above chemical equations results in the cancellation of the HS^{1-} ion concentration and eliminates it from the equilibrium constant expression. The equilibrium constant for the reaction that results from the addition of two equilibria equals the product of the two equilibrium constants, so we can write the following for the loss of both protons in one equation.



The above affords us a quick way to determine the concentration of sulfide ion in a solution where both the H_3O^{1+} and H_2S concentrations are known. However, the H_2S concentration is its equilibrium concentration, not its makeup concentration. Referring to Figure 7.4, we conclude that

- The above K_{12} expression is best used for solutions in which $\text{pH} < 5$, because above this pH , the H_2S concentration is no longer equal to the makeup concentration and would have to be determined with K_1 .

7.4-5. Exercise

EXERCISE 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 $\text{pH} = 3.00$?

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

(b) At what pH will the sulfide ion concentration be $1.0 \times 10^{-12}\text{ M}$?

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

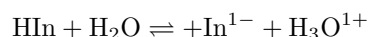
7.5 Acid-Base Indicators

Introduction

Acid-base indicators change color in small ranges of pH change and indicate the endpoint of an acid-base titration, but they too are weak acids and bases.

7.5-1. Acid-Base Indicators

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



The K_a expression is

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

Solving the above for the ratio of the concentrations of the base and the acid:

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

The human eye perceives the color of In^{1-} when the 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. Thus, 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 of the titration.** The following table gives the useful range of some common acid-base indicators.

Indicator	pH Range	Color Change
Methyl violet	0.0–1.6	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

Table 7.2: Some Common Indicators The pH range and color change of selected acid-base indicators.

7.5-2. Titration Exercise

EXERCISE 7.18:

The titration of 25.00 mL of a weak monoprotic acid HA requires 35.22 mL of 0.1095 M NaOH to reach the equivalence point. The pH of the solution was 5.26 after the addition of 20.00 mL of the base.

What is the concentration of HA in the original solution?

base added at the equivalence point = _____ mmol

HA in the original HA solution = _____ mmol

[HA] = _____ M

What is the pK_a of the acid?

A^{1-} present at the 20.00 mL point of the titration = _____ mmol

HA present at the 20.00 mL point of the titration = _____ mmol

if the pH at this point is 5.26, the pK_a = _____

What is the pH at the equivalence point?

the concentration of A^{1-} at the equivalence point is $[A^{1-}]$ = _____

the pK_b of A^{1-} is pK_b = _____

the K_b of A^{1-} is K_b = _____

the concentration of hydroxide at the equivalence point is $[OH^{1-}]$ = _____ M

the pH at the equivalence point is pH = _____

What indicator in Table 7.2 would be best to use for this titration? (Enter the first four letters.)

7.6 Exercises and Solutions

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