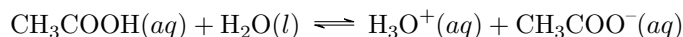


Buffer Calculations

A buffer is a solution that has the ability to resist a change in pH upon the addition of a strong acid or a strong base. For a buffer to exist it must satisfy two conditions: (1) the solution must contain a weak acid and its conjugate weak base, and (2) the concentrations of the weak acid and the conjugate weak base must be reasonably similar. This essay discusses in more detail how to calculate the pH of a buffer, how to evaluate the change in a buffer's pH after adding a strong acid or a strong base, and how to evaluate a buffer's capacity to neutralize a strong acid or a strong base.

The Standard Equilibrium Approach to Calculating a Buffer's pH

Thus far our standard approach to finding the pH of a solution is to write the equilibrium reaction responsible for controlling pH and use an ICE table to organize information. For example, to find the pH of a buffer that consists of 3.39×10^{-2} M CH_3COOH and 1.00×10^{-2} M CH_3COO^- , we first write the acid dissociation reaction for acetic acid



for which the equilibrium constant is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

Next, we use an ICE table to organize the problem

	$\text{CH}_3\text{COOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(l)$	+	$\text{CH}_3\text{COO}^-(aq)$
initial	3.39×10^{-2}		—		0		1.0×10^{-2}
change	$-X$		—		$+X$		$+X$
equilibrium	$3.39 \times 10^{-2} - X$		—		$+X$		$1.0 \times 10^{-2} + X$

Note that this table includes the initial concentrations for CH_3COOH and for CH_3COO^- , which were given to us, and assumes that we can ignore the presence of H_3O^+ from water (our standard assumption).¹ Defining the change in acetic acid's concentration as X , we then fill in the remainder of the table. Next, we substitute the terms in the row labeled "equilibrium" into the equilibrium constant expression.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(X)(1.0 \times 10^{-2} + X)}{3.39 \times 10^{-2} - X} = 1.8 \times 10^{-5}$$

To simplify the problem, we make the following two assumptions

$$3.39 \times 10^{-2} - X \approx 3.39 \times 10^{-2}$$

$$1.0 \times 10^{-2} + X \approx 1.0 \times 10^{-2}$$

Substituting these assumptions into the K_a expression and solving gives

¹Note, as well, that we ignore water, H_2O as it is not included in the equilibrium constant expression.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(X)(1.0 \times 10^{-2})}{3.39 \times 10^{-2}} = 1.8 \times 10^{-5}$$

$$X = 6.10 \times 10^{-5}$$

Before accepting this solution, we verify the assumptions by calculating the errors introduced into the calculation, finding that they are

$$\% \text{ error} = \frac{3.39 \times 10^{-2} - (3.39 \times 10^{-2} - 6.10 \times 10^{-5})}{3.39 \times 10^{-2}} \times 100 = +0.21\%$$

$$\% \text{ error} = \frac{1.0 \times 10^{-2} - (1.0 \times 10^{-2} - 6.10 \times 10^{-5})}{1.0 \times 10^{-2}} \times 100 = -0.6\%$$

Clearly our assumptions are within reason; thus, we know that $[\text{H}_3\text{O}^+] = X = 6.10 \times 10^{-5}$ and that the buffer's pH is 4.21.

The Henderson-Hasselbalch Equation

Now, let's look at buffers in a slightly different way. When we first introduced buffers in class we wrote the K_a expression in a logarithmic form called the Henderson-Hasselbalch equation. For an acetic acid/acetate buffer this equation is

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

There are two important things to note about this equation. First, the equation shows us that the pH of an acetic acid/acetate buffer is always at a pH level similar to acetic acid's $\text{p}K_a$ value. Given that K_a for CH_3COOH is 1.8×10^{-5} , the pH of an acetic acid/acetate buffer is always near

$$\text{pH} \approx \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

The actual pH will deviate from this, being more acidic when the concentration of CH_3COOH is greater than that for CH_3COO^- , and more basic when CH_3COO^- is present at a concentration greater than that for CH_3COOH .

For a buffer to exist the concentrations of the conjugate acid and the conjugate base cannot differ from each other by too much. As a guideline, we will adopt the following convention: a buffer exists when the relative amount of conjugate base-to-conjugate acid is within a range of 0.1–10

$$0.1 \leq \frac{\text{conjugate base}}{\text{conjugate acid}} \leq 10$$

Under these conditions, a buffer's pH falls within the limits

$$\text{p}K_a - 1 \leq \text{pH} \leq \text{p}K_a + 1$$

Another Way to Calculate a Buffer's pH

The Henderson-Hasselbalch equation provides us with a second method for calculating a buffer's pH. In our previous approach we used an ICE table to find the equilibrium concentrations of CH_3COOH , CH_3COO^- , and H_3O^+ in an acetic acid/acetate buffer. This led us to write

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(X)(1.0 \times 10^{-2} + X)}{3.39 \times 10^{-2} - X} = 1.8 \times 10^{-5}$$

where X is the equilibrium concentration of H_3O^+ . If we rewrite this in the form of the Henderson-Hasselbalch equation, we get

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]_o + [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]_o - [\text{H}_3\text{O}^+]}$$

where $[\text{CH}_3\text{COO}^-]_o$ and $[\text{CH}_3\text{COOH}]_o$ are, respectively, the initial concentrations of the acetate ion and acetic acid, and $[\text{H}_3\text{O}^+]$ is X . This equation leads us to a significant simplification that will apply to almost any buffer problem (or at least to problems in this course). Here is the simplification. As long as the $[\text{H}_3\text{O}^+]$ is much smaller than $[\text{CH}_3\text{COO}^-]_o$ or $[\text{CH}_3\text{COOH}]_o$, then we can drop the $[\text{H}_3\text{O}^+]$ terms, leaving us with the following equation in which all values except for the pH are known

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]_o}{[\text{CH}_3\text{COOH}]_o}$$

Why is this approximation so universal? Having defined a buffer as a solution whose pH level falls within the limits

$$\text{p}K_a - 1 \leq \text{pH} \leq \text{p}K_a + 1$$

we see that a buffer's smallest possible pH is $\text{p}K_a - 1$. This, in turn, defines the largest possible $[\text{H}_3\text{O}^+]$. For an acetic acid/acetate buffer, the smallest possible pH is 3.74 and the largest possible value for $[\text{H}_3\text{O}^+]$ is 1.8×10^{-4} . As long as we are willing to tolerate an error of 5% in our calculations, this means that the concentration of $[\text{H}_3\text{O}^+]$ is negligible as long as the initial concentrations of acetic acid or acetate are greater than

$$\frac{1.8 \times 10^{-4}}{0.05} = 0.0036 \text{ M}$$

Because the initial concentrations of acetic acid and acetate determine the buffer's ability to neutralize a strong base or acid (see further discussion below), it is unlikely that we would choose to work with an acetic acid/acetate buffer with concentrations this small. For an acid that is weaker than acetic acid, this minimum concentration is even smaller.

Having determined that we can calculate the pH using the equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]_o}{[\text{CH}_3\text{COOH}]_o}$$

we make one additional simplification. Because both CH_3COO^- and CH_3COOH are in the same solution, we can multiply their respective molar concentrations by the buffer's volume, V

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]_o \times V}{[\text{CH}_3\text{COOH}]_o \times V}$$

which simplifies to

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{(\text{moles CH}_3\text{COO}^-)_{\text{o}}}{(\text{moles CH}_3\text{COOH})_{\text{o}}}$$

This equation is nice because it allows us to calculate the buffer's pH without having to first calculate the concentrations of the buffering species. As we will see shortly, this is useful when we determine how the addition of a strong acid or a strong base will change a buffer's pH.

Example 1. What is the pH of a buffer prepared by dissolving 25.0 g of K_2HPO_4 and 25.0 g of KH_2PO_4 in 250 mL of water?

Solution. First, we determine which species is the weak acid and which is the conjugate weak base. Both compounds are ionic and will dissociate in water. The K^+ ions have no effect on the solution's pH, so we ignore them. The remaining anions are amphiprotic, meaning they have both acidic and basic properties. Because dihydrogen phosphate has one more proton than monohydrogen phosphate, H_2PO_4^- , is the weak acid. To find the pH of the resulting buffer, we find the initial moles of weak acid

$$25.0 \text{ g KH}_2\text{PO}_4 \times \frac{1 \text{ mol KH}_2\text{PO}_4}{136.1 \text{ g KH}_2\text{PO}_4} = 0.1837 \text{ mol H}_2\text{PO}_4^-$$

and the initial moles of weak base

$$25.0 \text{ g K}_2\text{HPO}_4 \times \frac{1 \text{ mol K}_2\text{HPO}_4}{174.2 \text{ g K}_2\text{HPO}_4} = 0.1435 \text{ mol HPO}_4^{2-}$$

Although the recipe contains information on the amount of water used to prepare the buffer, we don't need to include this in our calculation (although we will use it in the next example).

Knowing the moles of H_2PO_4^- and HPO_4^{2-} , we complete the calculation using the $\text{p}K_{\text{a}}$ value for H_2PO_4^- ; thus

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{(\text{mol HPO}_4^{2-})_{\text{o}}}{(\text{mol H}_2\text{PO}_4^-)_{\text{o}}} = 7.20 + \log \frac{0.1435}{0.1837} = 7.09$$

Finding a Buffer's pH After Adding a Strong Acid or Strong Base

When we add a strong base to a buffer it reacts with some of the conjugate weak acid and converts it into the conjugate weak base. For example, the following reaction takes place when we add a strong base, OH^- , to the buffer from the Example 1



Note we write this as a reaction that goes to completion. If you look at the reaction in reverse (from right-to-left), you will see that it is a weak base, HPO_4^{2-} , reacting with water to form its conjugate weak acid, H_2PO_4^- , and hydroxide ion, which is the standard form for a base dissociation reaction. The equilibrium constant for the reverse reaction, therefore, is K_{b} for HPO_4^{2-} , or 1.59×10^{-7} . This means the equilibrium constant for the reaction of H_2PO_4^- and OH^- is $(1.59 \times 10^{-7})^{-1}$ or 6.3×10^6 . Clearly the reaction essentially goes to completion.

Knowing that the reaction goes to completion makes it easy to find the moles of H_2PO_4^- and the moles of HPO_4^{2-} after the addition of OH^- ; these are

$$\text{moles H}_2\text{PO}_4^- = (\text{moles H}_2\text{PO}_4^-)_{\text{o}} - \text{moles OH}^-$$

$$\text{moles HPO}_4^{2-} = (\text{moles HPO}_4^{2-})_o + \text{moles OH}^-$$

Substituting into the Henderson-Hasselbalch equation gives

$$\text{pH} = \text{p}K_a + \log \frac{(\text{HPO}_4^{2-})_o + \text{moles OH}^-}{(\text{H}_2\text{PO}_4^-)_o - \text{moles OH}^-}$$

If we add a strong acid instead of a strong base, the result is

$$\text{pH} = \text{p}K_a + \log \frac{(\text{HPO}_4^{2-})_o - \text{moles H}_3\text{O}^+}{(\text{H}_2\text{PO}_4^-)_o + \text{moles H}_3\text{O}^+}$$

because adding H_3O^+ converts some of the HPO_4^{2-} to H_2PO_4^- .

Example 2. What is the pH if we add 10.00 mL of 1.00 M NaOH to the buffer from Example 1?

Solution. The moles of NaOH added is

$$10.00 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mol OH}^-}{1 \text{ L NaOH}} = 0.0100 \text{ mol OH}^-$$

Substituting into the Henderson-Hasselbalch equation gives

$$\text{pH} = \text{p}K_a + \log \frac{(\text{HPO}_4^{2-})_o + \text{moles OH}^-}{(\text{H}_2\text{PO}_4^-)_o - \text{moles OH}^-} = 7.20 + \log \frac{0.1435 + 0.0100}{0.1837 - 0.0100} = 7.15$$

Note that adding NaOH raises the pH by just 0.06 pH units, demonstrating that the buffer can neutralize a strong base with only a small change in pH. Adding a similar quantity of NaOH to an equivalent amount of water (250.0 mL) gives

$$[\text{OH}^-] = \frac{\text{moles NaOH}}{\text{total volume}} = \frac{0.0100 \text{ mol}}{0.250 \text{ L} + 0.0100 \text{ L}} = 0.0385 \text{ M}$$

or a pOH of 1.41 and a pH of 12.59. With the water initially at a pH of 7 (neutral), the change in pH for this unbuffered solution is 5.59 pH units.

Evaluating a Buffer's Capacity

Adding a strong acid or a strong base slowly destroys a buffer's ability to do its job because the ratio

$$\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

in the Henderson-Hasselbalch equation changes. Once this ratio falls outside range of 0.1 to 10 a buffer ceases to exist. We define a buffer's buffer capacity as the moles of strong acid or strong base the buffer can neutralize before it reaches the end of its range.² When we add a strong acid this means that the buffer capacity is defined by the equation

$$\frac{(\text{moles weak base})_o - \text{moles H}_3\text{O}^+}{(\text{moles weak acid})_o + \text{moles H}_3\text{O}^+} = 0.1$$

²There is a more quantitatively accurate description of buffer's maximum capacity; however, in the context of this course, this definition is sufficient.

and when we add a strong base the buffer capacity is defined by the equation

$$\frac{(\text{moles weak base})_o + \text{moles OH}^-}{(\text{moles weak acid})_o - \text{moles OH}^-} = 10$$

Example 3. How many mL of 6.0 M NaOH can we add to the buffer in Example 1 before it reaches its limit?

Solution. Letting the moles of NaOH be X , we write

$$\frac{(\text{HPO}_4^{2-})_o + \text{moles OH}^-}{(\text{H}_2\text{PO}_4^{2-})_o - \text{moles OH}^-} = \frac{0.1435 + X}{0.1837 - X} = 10$$

$$0.1435 + X = 1.837 - 10X$$

$$11X = 1.6935$$

$$X = 0.154 \text{ mol NaOH}$$

This corresponds to a volume of 6.0 M NaOH equal to

$$0.154 \text{ mol NaOH} \times \frac{1 \text{ L}}{6.0 \text{ mol NaOH}} \times \frac{1000 \text{ mL}}{\text{L}} = 25.7 \text{ mL}$$

Thus, we can add 25.7 mL of 6.0 M NaOH before we exceed the buffer's capacity to neutralize strong base.

At times we need to define a buffer's capacity more narrowly. In Example 1 we showed that a solution that contains 0.1837 moles of H_2PO_4^- and 0.1435 moles of HPO_4^{2-} has a pH of

$$\text{pH} = \text{p}K_a + \log \frac{(\text{mol HPO}_4^{2-})_o}{(\text{mol H}_2\text{PO}_4^-)_o} = 7.20 + \log \frac{0.1435}{0.1837} = 7.09$$

The buffer's maximum capacity to neutralize strong acid is set by the buffer's lower pH limit of 6.20 ($\text{p}K_a - 1$). Suppose, however, that for a particular experiment the buffer's pH must not fall below 6.90. Example 4 shows how to determine this more narrowly defined buffer capacity.

Example 4. How many moles of strong acid can the buffer in Example 1 absorb without the pH drifting below 6.90?

Solution. When we add a strong acid to a buffer the relevant form of the Henderson-Hasselbalch equation is

$$\frac{(\text{moles HPO}_4^{2-})_o - \text{moles H}_3\text{O}^+}{(\text{moles H}_2\text{PO}_4^-)_o + \text{moles H}_3\text{O}^+}$$

Letting X be the moles of H_3O^+ and substituting known values for the $\text{p}K_a$ of H_2PO_4^- and the moles of H_2PO_4^- and HPO_4^{2-} gives

$$6.90 = 7.20 + \log \frac{0.1435 - X}{0.1837 + X}$$

$$-0.30 = \log \frac{0.1435 - X}{0.1837 + X}$$

$$0.5012 = \frac{0.1435 - X}{0.1837 + X}$$

$$0.09207 + 0.5012X = 0.1435 - X$$

$$1.5012X = 0.05143$$

$$X = 3.43 \times 10^{-2} \text{ mol H}_3\text{O}^+$$

Thus, the buffer capacity for this scenario is 3.43×10^{-2} moles of strong acid.