

9.2: Buffered Systems

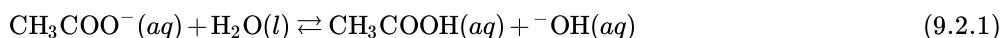
When you think of the word buffer, you probably think of it as a safeguard or a barrier—something that provides a cushion or shield between you and something harmful. But in chemistry and biology, a buffer is a solution that resists changes in pH. As we will soon learn, this ability is critical to all living systems. Many reactions are affected by changes in pH. For example, strong acid and base solutions are harmful to living tissue because they cause rapid hydrolysis of the bonds that hold living organisms together. That is, acidic or basic solutions can speed up the reactions in which the bonds are broken (dead bodies are often disposed of in murder mysteries—and sometimes in real life—by dissolving them in strong acid or base). Proteins have many weak acid and base groups, and so even relatively small fluctuations in pH can cause changes in the charges of these groups. This can affect protein structure and function dramatically, in a way that is physiologically damaging to living systems.

Aqueous solution chemistry is terrifically complicated in living systems. However, we can begin to understand it by looking at simple chemical buffer systems. Let us first consider what happens if we take 0.10 moles of hydrogen chloride gas and dissolve it in enough water to make one liter of solution. The resulting 0.10 M solution of hydrochloric acid $\text{HCl}(aq)$ has a pH of 1 ($\text{pH} = -\log(0.10) = -\log(1.0 \times 10^{-1})$). So the pH of the solution changes from 7 (for pure water) to 1, a change of 6 orders of magnitude in $[\text{H}^+]$. Now, if we do the same experiment adding 0.10 mol $\text{HCl}(g)$ to an appropriately buffered solution, we find the pH of the resulting solution does not change very much at all.

To understand how this happens, we have to review some acid–base chemistry. Specifically, we must reexamine what happens when acids and base react, what the products are, and how those products behave. We just calculated that the pH of a 0.10 M strong acid is 1.0. It does not matter which strong acid we choose, as long as it only has one proton to donate. So the pH of solutions HCl , HBr , and HClO_4 are all the same because they are all almost completely ionized in aqueous solution. However, what happens if we use a weak acid like acetic acid (CH_3COOH), hydrogen fluoride (HF), phosphoric acid (H_3PO_4), or carbonic acid (H_2CO_3)? The pH of each differs and none of them is as low as the strong acids because they do not ionize completely in solution. For example, the pH of 0.10 M acetic acid is ~ 2.9 because the concentration of H^+ is lower than in 0.10 M HCl . Although that may not seem very different from a pH of 1, remember that $[\text{H}^+]$ is 10^{-1} (or 0.1 M) for a pH of 1 and $10^{-2.9}$ (or 0.0012 M) for a pH 2.9.

Now if we look at the conjugate bases of weak and strong acids we will see an analogous difference in their behavior to produce solutions with different pH's. The conjugate base of HCl is Cl^- (the chloride ion.) However since we can't just get a bottle of chloride (we need a counter ion for charge balance), we will use sodium chloride, NaCl , since we know that sodium ions are not reactive, they are usually “spectator” ions. If we measure the pH of a solution of NaCl , we will find that it is 7, just like water. Neither the sodium ion nor the chloride ion affects the pH. However, if we take the corresponding conjugate base from acetic acid, for example sodium acetate (CH_3COONa), we find that a 0.1 M solution has a pH of about 9. This is quite surprising at first glance. Sodium acetate belongs to the class of compounds that we label generically as salts. In everyday life, salt refers to sodium chloride, but in chemistry the term salt refers to a compound that contains the conjugate base of an acid and a cation. Although it is tempting to think of all salts as innocuous and unreactive (like sodium chloride), it turns out that components of the salt (the conjugate base anion, and the cation) both affect the properties, even in a simple reaction like dissolving in water. In fact, the pH of any conjugate base of a weak acid tends to be basic.

Let us investigate a bit further. The previous observation implies that the acetate ion (CH_3COO^-) must be reacting with water to produce hydroxide (since we already know the Na^+ does not react with water). This reaction is called a hydrolysis reaction. The name is derived from the Greek words for water (hydro-) and to break or separate (-lysis); it refers to reactions in which water is one of the reactants. We can write this hydrolysis reaction as:



The production of hydroxide increases $[\text{OH}^-]$, in turn affects $[\text{H}^+]$ because the two are related by the equilibrium expression $[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} = K_w$. In other words, when the salt of a weak acid (that is, its conjugate base) is dissolved in water, a weak base is produced and that weak base has all the properties of any base: it can react with an acid.

It is possible to calculate the pH of weak base solutions, just as it is to calculate the pH of weak acids, if you know the acid equilibrium constant.^[6] However, what is more interesting is what happens when a solution contains significant amounts of both a weak acid and its conjugate base. For example, if we take a solution that is 0.10 M in both acetic acid and sodium acetate, we can calculate the pH by setting up the equilibrium table:

AcOH	+H ₂ O	\rightleftharpoons H ₃ O ⁺	+ ⁻ OAc	+ Na ⁺
Initial concentrations 0.10 M		1×10^{-7}	0.10 M	0.10 M

Note that even though acetate is present in the initial mixture, we have put it on the product side. This is because when both acetic acid and acetate are present in the same solution, their concentrations are “linked”: they become part of an equilibrium system that can be described by the equilibrium constant for acetic acid.^[7] If the concentration of one species is changed, the other must respond. Recall in Chapter 8 that we looked at what happens to the pH of a solution of acetic acid when an acetate ion is added: the presence of acetate affects the position of equilibrium for the acetic acid dissociation, and instead of a pH of 2.9 (for 0.10 M acetic acid), the pH of a solution that is 0.10 M in both acetic acid and sodium acetate is 4.7. The presence of the common ion acetate has suppressed the ionization of acetic acid. We can calculate the pH of any similar solution by adapting the expression for the acid dissociation equilibrium:

$$K_a = [\text{H}^+] [\text{AcO}^-] / [\text{AcOH}]. \quad (9.2.2)$$

As in our previous work with weak acids we are going to ignore any reaction with water from both the acetic acid and the acetate ion because they do not affect the pH significantly; both species are relatively weak as acids or bases. Even if we take these reactions into account, they do not change the answer we get. Substituting in the equation for K_a , we get:

$$K_a = 1.8 \times 10^{-5} = [\text{H}^+] (0.10)/(0.10). \quad (9.2.3)$$

Alternatively, we can use $\text{p}K_a$, the negative log of K_a , giving us:

$$\begin{aligned} \text{p}K_a &= \text{pH} - \log [\text{AcO}^-] / [\text{AcOH}] \\ \text{or pH} &= \text{p}K_a + \log [\text{AcO}^-] / [\text{AcOH}]. \end{aligned}$$

This equation is known as the Henderson–Hasselbalch equation. It is a convenient way to calculate the pH of solutions that contain weak acids and their conjugate bases (or weak bases and their conjugate acids).

Recall that a buffer can resist changes in pH. So the question is: how exactly does this happen? Let us take a closer look. Imagine we have a buffer solution that is 1.0 M in both acetic acid and acetate. The pH of this system is $-\log 1.8 \times 10^{-5} = 4.74$ (because $[\text{AcO}^-] = [\text{AcOH}]$). Now let us add some acid to this buffer. To make calculations easy, we can add 0.01 mol HCl to 1.0 L of buffer solution.^[8] What happens? The major species in the buffer solution are acetic acid, acetate, and water (hydronium ion and hydroxide ion are minor components). Which one will react with HCl(aq)? Just as in any acid–base reaction, it is more likely that the base will react with the acid that is, the acetate part of the buffer will react with the H⁺. The resulting reaction is:



In this reaction, the acetate concentration decreases and the acetic acid increases. We can now calculate the initial (pre-reaction) and final (post-reaction) concentrations:

	AcOH	+ H ₂ O	\rightleftharpoons H ₃ O ⁺	+ ⁻ OAc
Initial [M]	1.00		(negligible)	1.00
add 0.01 M H ⁺⁺	+0.01			–0.01
Equilibrium [M]	1.01		x	0.99

The pH of this system can be calculated from the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log(0.99/1.01) = 4.73. \quad (9.2.5)$$

The pH has hardly budged! (Recall that the pH of 0.01 M HCl is 2.0.) Even if we add more acid (say, 0.1 mol HCl) to our liter of buffer, the resulting pH does not change much (it is $\text{pH} = 4.74 + \log(0.90/1.10) = 4.65$). Note that the addition of acid has moved the pH in the direction we would expect—slightly lower and more acidic but nowhere near what it would be if we had added the HCl directly to 1 L of water.

We can also look at what happens when we add a strong base to the buffer solution. If we add 0.01 mol sodium hydroxide to our liter of buffer, the “active” component of the buffer is now the acid, and the reaction is written: $\text{HOAc} + ^-\text{OH} \rightleftharpoons \text{AcO}^- + \text{H}_2\text{O}$.

The strong base reacts with the weak acid. The acid concentration falls and its conjugate base concentration rises, so:

	AcOH	+ H ₂ O	$\rightleftharpoons \text{H}_3\text{O}^+$	+ ⁻ OAc
Initial [M]	1.00		(negligible)	1.00
add 0.01 M ⁻ OH	-0.01			+0.01
Equilibrium [M]	0.99		<i>x</i>	1.01

The new pH of the solution is $\text{pH} = 4.74 + \log(1.01/0.99) = 4.75$ —a slight increase but hardly detectable. (Note that the pH of a 0.01 M solution of NaOH is 12.)

So, buffers can keep the pH of a solution remarkably constant. – which, as we will see, this is very important for biological systems. But this raises another question, just how much acid could we add to the system before the pH did change appreciably, or rather, enough to influence the behavior of the system? In biological systems, the tolerance for pH change is fairly low. As we discussed previously, changes in pH can cause a cascade of reactions that may prove catastrophic for the organism.

The amount of acid or base that a buffer solution can absorb is called its buffering capacity. This capacity depends on the original concentrations of conjugate acid and base in the buffer and their ratio after reaction, or [conjugate acid]/[conjugate base]. If you start with a buffer that has equal amounts of acid and base, the ratio is equal to 1.0. As the ratio moves further away from 1.0, the pH is affected more and more, until it changes out of the desired range.

Another important property of buffers is the range of pH that they can act over. As we have seen from the Henderson–Hasselbalch equation, when the concentration of acid is equal to the concentration of base, the pH of the solution is equal to the pK_a of the acid. Thus, the acetic acid/acetate buffer has a $\text{pH} = 4.74$. Generally, the effective buffering range is +1 or –1 pH unit around the pK_a . So the acetic acid/acetate acts as an effective buffer in the range of $\text{pH} 3.7 - 5.7$, well within the acidic pH region. There are biological compartments (the stomach, lysosomes, and endosomes) that are acidic but the major biological fluids (cytoplasm and blood plasma) have pH's around 7.2–7.4. In these systems, buffers are phosphate or carbonate systems. For example, the phosphate buffer system is composed mainly of H_2PO_4^- (the proton donor or acid), and HPO_4^{2-} (the proton acceptor or base):



What counts as an acid or a base depends entirely on the reaction system you are studying. This is an important point. Both H_2PO_4^- and HPO_4^{2-} can act as either an acid or a base depending on the pH. (Try writing out the reactions.) But at physiological pH(7.2 – 7.4), the predominant forms are H_2PO_4^- and HPO_4^{2-} . The pK_a of the conjugate acid is 6.86 so it makes sense that this buffer system is active in cellular fluids.

Questions

Questions to Answer

- How much acid would you have to add to change the pH of a buffer that is 1.0 M in acid and conjugate base by one full pH unit?
- If the buffer is 0.1 M in acid and conjugate base, would you have to add the same amount of acid? Why or why not?
- What buffer systems would you use to buffer a pH of 4, 6, 8, and 10? What factors would you take into account?
- Carbonic acid (H_2CO_3) has two acidic protons. Draw out the structure of carbonic acid, and show how each proton can take part in an acid–base reaction with a strong base such as sodium hydroxide.
- What is the pH of a buffer system if the concentration of the acid component is equal to the concentration of its conjugate base?
- Can any buffer system buffer any pH? For example, could an acetic acid/acetate system effectively buffer a pH of 9?
- What criteria would you use to pick a buffer system for a particular pH?

Questions to Ponder

- What factors might make reactions sensitive to pH?
- Why are protein structure and activity sensitive to changes in pH?

- Which parts of proteins are affected by changes in pH? What kinds of chemical properties must they have? What groups of atoms do these bits of proteins contain?
- Would you expect nucleic acids to be more or less sensitive to pH changes than proteins?

This page titled [9.2: Buffered Systems](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Melanie M. Cooper & Michael W. Klymkowsky](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.