

Buffered Solutions

How Buffers Work

As you have seen in calculating the pH of solutions, only a small amount of a strong acid is necessary to drastically alter the pH. For certain experiments, however, it is desirable to keep a fairly constant pH while acids or bases are added to the solution either by reaction or by the experimenter. Buffers are designed to fill that role. Chemists use buffers routinely to moderate the pH of a reaction. Biology finds manifold uses for buffers which range from controlling blood pH to ensuring that urine does not reach painfully acidic levels.

A buffer is simply a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. Buffers work by reacting with any added acid or base to control the pH. For example, let's consider the action of a buffer composed of the weak base ammonia, NH_3 , and its conjugate acid, NH_4^+ . When HCl is added to that buffer, the NH_3 "soaks up" the acid's proton to become NH_4^+ . Because that proton is locked up in the ammonium ion, it proton does not serve to significantly increase the pH of the solution. When NaOH is added to the same buffer, the ammonium ion donates a proton to the base to become ammonia and water. Here the buffer also serves to neutralize the base.

As the above example shows, a buffer works by replacing a strong acid or base with a weak one. The strong acid's proton is replaced by ammonium ion, a weak acid. The strong base OH^- was replaced by the weak base ammonia. These replacements of strong acids and bases for weaker ones give buffers their extraordinary ability to moderate pH.

Calculating the pH of Buffered Solutions

Buffers must be chosen for the appropriate pH range that they are called on to control. The pH range of a buffered solution is given by the Henderson- Hasselbalch equation. For the purpose of the derivation, we will imagine a buffer composed of an acid, HA, and its conjugate base, A^- . We know that the acid dissociation constant K_a of the acid is given by this expression:

Figure 1.1

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The equation can be rearranged as follows:

Figure 1.2

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

Taking the -log of this expression and rearranging the terms to make each one positive gives the Henderson-Hasselbalch equation:

Figure 1.3

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

Figure 1.3: The Henderson-Hasselbalch Equation

Note that the sample species HA and A⁻ in the above Expression are generalized to the terms acid and base, respectively. To use the equation, place the concentration of the acidic buffer species where the equation says "acid" and place the concentration of the basic buffer species where the equation calls for "base". It is essential that you use the pK_a of the acidic species and not the pK_b of the basic species when working with basic buffers--many students forget this point when doing buffer problems.

A buffer problem can be fairly simple to solve, provided you don't get confused by all the other chemistry you know. For example, let's calculate the pH of a solution that is 0.5 M acetic acid and 0.5 sodium acetate both before and after enough SO₃ gas is dissolved to make the solution 0.1 M in sulfuric acid. Before the acid is added, we can use the Henderson-Hasselbalch equation to calculate the pH.

Figure 1.4

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$
$$\text{pH} = 4.75 + \log \left(\frac{[0.5 \text{ M}]}{[0.5 \text{ M}]} \right)$$
$$\text{pH} = 4.75$$

Figure 1.4: Note that the pK_a of acetic acid is 4.75.

This part of the problem does not require us to do the sort of equilibrium calculations that we must use for **Non-Buffered Solutions**, but many students still try to do it the hard way. The hard way is a correct way of doing the problem, but it may cost you valuable time on a test.

To calculate the pH after the acid is added, we assume that the acid reacts with the base in solution and that the reaction has a 100% yield. Therefore, we say that 0.1 moles per liter of acetate ion reacts with 0.1 moles per liter of sulfuric acid to give 0.1 moles per liter of acetic acid and hydrogen sulfate. Here, we ignore the second dissociation of sulfuric acid because it is minor in comparison to the first. So the final concentration of acetic acid is 0.6 M and acetate is 0.4M. Plugging those values into the Henderson-Hasselbalch equation gives a pH of 4.57. Note that a 0.1 M solution of strong acid would give to a pH of 1 but the buffer gives a pH of 4.57 instead.

To probe the useful range of the buffer, let's calculate the pH of the solution resulting from the same situation above but with different concentrations of the buffer. If the buffer is 1.0 M in both acetate and acetic acid, then the pH of the resulting solution after the introduction of acid is 4.66. However, if we make the solution only 0.11 M in acetic acid and acetate, then we calculate a pH of 3.45! Therefore, if you want a more effective buffer, make sure that the concentration of the buffering agents is large in comparison to the added acid or base.