



# 11

## Buffer Solutions

### Introduction

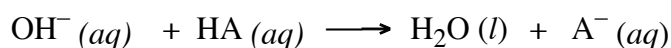
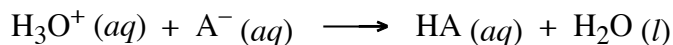
Any solution that contains both a weak acid HA and its conjugate base  $A^-$  in significant amounts is a buffer solution. A buffer is a solution that will tend to maintain its pH when small amounts of either acid or base are added to it. Buffer solutions can be made to maintain almost any pH, depending on the acid-base pair used. The pH of a buffer solution is determined by the  $K_a$  of the acid and by the ratio of concentrations of HA and  $A^-$ . This can be calculated by rearranging the expression for the  $K_a$  of the conjugate acid of the buffer:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{becomes} \quad [H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

The rearranged equation shows that the  $H_3O^+$  ion concentration of the buffer solution can be found by multiplying the  $K_a$  of the acid by the ratio of the molar concentrations of the two components. To solve directly for the pH of the buffer, the equation can be put into logarithmic form. If the above equation is rearranged and the negative log of both sides is taken, a new form of the equation known as the Henderson-Hasselbalch equation results.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad \text{Henderson-Hasselbalch equation}$$

A buffer solution can maintain its approximate pH when an acid or a base is added to it because it can react with both acids and bases. If a strong acid ( $H_3O^+$ ) is added, the basic component of the buffer ( $A^-$ ) can react with it, and if a strong base ( $OH^-$ ) is added, the acidic component of the buffer (HA) will react with it.



In this way, any strong acid or strong base that is added to the buffer solution is converted into a weak acid or weak base. The ratio of weak acid to weak base changes, which causes the pH to change slightly, but not drastically.

Buffer solutions are most effective when both components, the conjugate acid and the conjugate base, are present in reasonably large concentrations. If this is the case, the buffer is said to have a high buffer capacity. Also, a buffer is most effective when there are approximately equal concentrations of the two buffer components (a ratio of  $[X^-]/[HX]$  close to 1/1) because in this case the solution will guard against large pH changes equally well whether acid is added or base is added.

In order for the solution to be considered a buffer, this ratio must be between a 1/10 and a 10/1 ratio of  $[X^-]/[HX]$ . This restriction means that the  $[H_3O^+]$  in the buffer will be within a factor of 10 of the  $K_a$  value of the conjugate acid. It also means that the pH of the buffer will be within one pH unit of the value of the  $pK_a$  of the conjugate acid. For example, suppose you wanted to make a buffer containing phosphoric acid ( $H_3PO_4$ ) and dihydrogen phosphate ( $H_2PO_4^-$ ). Since the  $K_a$  of  $H_3PO_4$  is  $7.5 \times 10^{-3}$  and the  $pK_a$  is 2.12, as shown in the table below, the pH of this buffer would have to be between 1.12 and 3.12. If you wanted to make a buffer with a pH outside of this range, you would have to choose a different conjugate acid-base pair.

*Buffer Solutions That Can Be Made With  $H_3PO_4$  and  $H_2PO_4^-$*

$K_a$	$pK_a$	$\frac{[H_2PO_4^-]}{[H_3PO_4]}$	$[H_3O^+] = K_a \frac{[H_3PO_4]}{[H_2PO_4^-]}$	$pH = pK_a + \log \frac{[H_2PO_4^-]}{[H_3PO_4]}$
$7.5 \times 10^{-3}$	2.12	1/10	$7.5 \times 10^{-2}$	1.12
		1/1	$7.5 \times 10^{-3}$	2.12
		10/1	$7.5 \times 10^{-4}$	3.12

In this experiment, you will be assigned a pH value, and you will prepare a buffer solution having that pH. There will be two sets of acid-base pairs available in the lab. These are:

1. Acetic acid ( $CH_3CO_2H$ ,  $K_a = 1.8 \times 10^{-5}$ ) and sodium acetate ( $NaC_2H_3O_2$ ).
2. Ammonium chloride ( $NH_4Cl$ ,  $K_a$  for  $NH_4^+ = 5.6 \times 10^{-10}$ ) and ammonia ( $NH_3$ ).

The buffer will be prepared by choosing the appropriate acid-base pair, calculating the molar ratio of acid to base that will produce the assigned pH, and then mixing the calculated amounts of the two compounds with enough deionized water to make 200. mL of buffer solution.

A solution with approximately the same pH as the buffer solution will be prepared by diluting a solution of a strong acid or a strong base. This solution will not be a buffer solution, as can be shown by comparing its buffering ability to that of the buffer solution. Finally, a known amount of strong acid or base will be added to the buffer solution. Before adding this acid or base, the pH change that the addition should cause will be calculated. The observed pH change will be compared to the calculated value.

## Experimental Procedure

**SAFETY PRECAUTIONS:** Wear your SAFETY GOGGLES. Use the concentrated acetic acid and ammonia solutions in the FUME HOOD. If any acid or base solution splashes on your skin, wash it off immediately with copious amounts of running water.

**WASTE DISPOSAL:** All waste from this experiment should be poured down the drain, followed by plenty of running water.

### *Part 1 - Preparing the Buffer Solution*

#### *Prelab Calculations*

1. Obtain a pH assignment from your instructor.
2. Decide which of the two available buffer systems you should use.
3. Determine the ratio of  $[A^-]/[HA]$  needed in the buffer.
4. Which component will be more concentrated,  $A^-$  or  $HA$ ? Choose a value for the concentration of that component anywhere in the range 0.2 – 0.6 M. Calculate what the concentration of the other component should be.
5. Calculate the volume (in mL) of 17.5 M  $CH_3CO_2H$  or 14.8 M  $NH_3$  needed to make 200 mL of your buffer. Calculate the mass (in g) of solid  $NaCH_3CO_2 \cdot 3H_2O$  or  $NH_4Cl$  needed to make 200 mL of your buffer.

#### *Procedure*

Measure out the amounts of the buffer components needed, add them to about 100 mL of deionized water in a 250-mL Erlenmeyer flask. Swirl until all the solids are dissolved. Pour the mixture into a large graduated cylinder, and dilute it to a total volume of 200 mL. Pour it back and forth between the graduated cylinder and your flask so that it is thoroughly mixed. Store the buffer solution in the flask.

Set up a pH meter at your desk and calibrate it according to the instructions. Remember that the electrode of the pH meter is FRAGILE! Also, remember to rinse the electrode off with deionized water when transferring it between different solutions.

Pour about 50 mL of your buffer solution into a small beaker and measure the pH. The pH of the solution should be close to the expected value but might not be exactly the same. A minor discrepancy will not affect the results of the remainder of the experiment.

There are several possible reasons for the pH meter reading being different from the expected pH. One is that some of the volatile component of your buffer may have escaped from the solution into the air. Another is the fact that the  $K_a$  values for acids vary with temperature. The values usually reported are accurate for 25°C.

### *Part 2- Preparing a Solution with the Same pH by Dilution of a Strong Acid or Base*

The pH of a typical acetic acid-acetate buffer solution is between 4 and 5. A solution with a pH in this range can easily be prepared by diluting a solution of strong

acid, such as HCl, until the hydronium ion concentration is between  $10^{-4}$  and  $10^{-5}$  M. Similarly, a typical ammonium ion-ammonia buffer solution has a pH between 9 and 10. A dilute solution of NaOH with  $[\text{OH}^-]$  between  $10^{-4}$  and  $10^{-5}$  M will also be in this pH range. These solutions, however will not act as buffer solutions. In this section of the experiment, you will prepare a solution with approximately the same pH as your buffer solution by diluting a more concentrated solution of strong acid or base.

#### *Prelab Calculations*

If your buffer is acidic, calculate the volume (in mL) of 0.0010 M HCl needed to prepare 100 mL of a solution that has the same pH as your buffer.

If your buffer is basic, calculate the volume (in mL) of 0.0010 M NaOH needed to prepare 100 mL of a solution that has the same pH as your buffer.

#### *Procedure*

Prepare your unbuffered solution, by diluting the calculated amount of 0.0010 M HCl or 0.0010 M NaOH solution to a final volume of 100 mL. Measure its pH. Again, the reading on the pH meter may not display the pH expected for the solution. The pH of solutions as dilute as this can be affected by small amounts of impurities, including  $\text{CO}_2$  dissolved in the water. The pH can be adjusted if desired, but the comparison of this solution to the buffer solution will work even if the pH values of the two are not the same.

### ***Part 3 - Comparing the Buffering Abilities of the two Solutions***

#### *Procedure*

To test the buffering abilities of the solutions, 0.1 M HCl or 0.1 M NaOH will be added. If the solutions are acidic, add 0.1 M NaOH, and if they are basic, add 0.1 M HCl.

Place the pH electrode in the 50 mL of buffer solution tested earlier. Re-measure the pH, then add 5 drops of 0.1 M NaOH or 0.1 M HCl solution (see above). Carefully swirl the solution, making sure not to bump the electrode, and record the new pH. Repeat the procedure with another 5 drops of NaOH or HCl. How much did the pH change upon the addition of these amounts of HCl or NaOH?

Rinse off the electrode with deionized water, place it in the nonbuffered solution, and measure the pH. Follow the same procedure as you used for the buffer solution. Add 5 drops of drops of HCl or NaOH, and record the new pH. Add 5 more drops, and record the pH. It is important to follow the same procedure so that you can more accurately compare the two solutions. How much did the pH change for the unbuffered solution? How do the pH changes compare for the buffered and unbuffered solutions?

### ***Part 4 - Changing the pH of a Buffer Solution***

The pH of a buffer solution does change when large amounts of strong acid or strong base are added to it. Addition of strong acid uses up the conjugate base of the

buffer, and addition of strong base uses up the conjugate acid. The pH of the buffer changes because the ratio of conjugate acid to conjugate base has been changed.

In this part of the experiment, enough 1.0 M HCl will be added to 100. mL of the buffer solution to react with half of the conjugate base in the solution. The observed change in pH will be compared to the pH change expected on the basis of the prelab calculation.

### *Prelab Calculations*

1. How many moles of base ( $\text{NH}_3$  or  $\text{C}_2\text{H}_3\text{O}_2^-$ ) are in 100 mL of the buffer solution you prepared? What is half of this amount? This is the number of moles of HCl that you will add to the solution.
2. Calculate the volume (in mL) of 1.0 M HCl needed to supply this number of moles. That is the amount needed to react with half of the conjugate base in 100 mL of your buffer solution.
3. What should the pH be after this amount of HCl is added? What is the expected change in pH of the buffer?

### *Procedure*

Add this volume of 1.0 M HCl to 100 mL of the buffer solution, and measure the pH. Record the change in pH. Compare the expected (calculated) pH change to the actual pH change of the buffer.

## **Sample Calculations**

### ***Part 1 – Preparing a Buffer Solution***

Sample calculations will be done for an assigned pH of 2.50.

A pH of 2.50 corresponds to a  $[\text{H}_3\text{O}^+] = 10^{-2.50} = 3.162 \times 10^{-3}$  M. Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) could be used to make this buffer, because  $K_a$  for  $\text{H}_3\text{PO}_4$  ( $K_a = 7.5 \times 10^{-3}$ ) is close to the desired  $[\text{H}_3\text{O}^+]$ .

$$\text{The } \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \text{ ratio should be } \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{7.5 \times 10^{-3}}{3.162 \times 10^{-3}} = \frac{2.372}{1}$$

$\text{H}_2\text{PO}_4^-$  will be the most concentrated component of this buffer system. We will arbitrarily choose its concentration to be 0.50 M. This means that the concentration of  $\text{H}_3\text{PO}_4$  should be  $0.50 \text{ M} \div 2.372 = 0.2108 \text{ M}$

To make 200 mL of the buffer solution, we will need to measure out a certain volume of concentrated phosphoric acid, which is available as a 14.7 M aqueous solution. And we will need to weigh out a certain mass of sodium dihydrogen phosphate, which is available as the hydrated solid,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  (the waters of hydration are included in the molar mass).

To make 200 mL of a 0.2108 M phosphoric acid solution,

$$200 \text{ mL} \times \frac{0.2108 \text{ M}}{14.7 \text{ M}} = 2.87 \text{ mL of concentrated phosphoric acid needed.}$$

To make 200 mL of a 0.50 M sodium dihydrogen phosphate solution,

$$0.200 \text{ L} \times \frac{0.50 \text{ mol}}{\text{L}} \times \frac{156.0 \text{ g}}{\text{mol}} = 15.60 \text{ g of NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O needed.}$$

So, to prepare the buffer solution, we will mix 2.87 mL of concentrated  $\text{H}_3\text{PO}_4$  and 15.60 grams of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  with enough water to make 200 mL of solution.

### **Part 2- Preparing a Solution with the Same pH by Dilution of a Strong Acid or Base**

To make 100 mL of a solution with  $\text{pH} = 2.50$  ( $[\text{H}_3\text{O}^+] = 3.162 \times 10^{-3} \text{ M}$ ), we will dilute a 0.10 M HCl solution. (Note, in your experiment, you will be diluting an 0.0010 M HCl solution or an 0.0010 M NaOH solution.)

$$100 \text{ mL} \times \frac{3.162 \times 10^{-3} \text{ M}}{0.10 \text{ M}} = 3.16 \text{ mL of 0.10 M HCl needed}$$

So, to prepare the unbuffered solution, we will mix 3.16 mL of 0.10 M HCl with enough water to make 100 mL of solution.

### **Part 4 - Changing the pH of a Buffer Solution**

We will take 100 mL of the buffer solution, and add enough 1.0 M HCl to react with half of the moles of  $\text{H}_2\text{PO}_4^-$ , the conjugate base.

$$0.100 \text{ L} \times \frac{0.50 \text{ mol}}{\text{L}} = 0.050 \text{ moles of } \text{H}_2\text{PO}_4^- \text{ are present in 100 mL}$$

0.025 moles of  $\text{H}_2\text{PO}_4^-$  will be react with 0.025 moles of HCl.

$0.025 \text{ mol HCl} \times \frac{\text{L}}{1.0 \text{ mol}} = 0.025 \text{ L or 25 mL of 1.0 M HCl will be added.}$

So, to change the pH of our buffer solution, we will take 100 mL of our original buffer solution, and add 25 mL of 1.0 M HCl to it.

All of the added HCl will react with the  $\text{H}_2\text{PO}_4^-$ . Some  $\text{H}_2\text{PO}_4^-$  will be used up, and more  $\text{H}_3\text{PO}_4$  will be formed.

	$\text{H}_3\text{O}^+ (aq)$	$+ \text{H}_2\text{PO}_4^- (aq)$	$\longrightarrow$	$\text{H}_3\text{PO}_4 (aq)$	$+ \text{H}_2\text{O} (l)$
Before reaction	0.025 mol	0.050 mol		0.021 mol	lots
	<u>-0.025 mol</u>	<u>-0.025 mol</u>		<u>+0.025 mol</u>	
After reaction	0	0.025 mol		0.046 mol	

$$[\text{H}_3\text{O}^+] = K_a \frac{(\text{moles } \text{H}_3\text{PO}_4)}{(\text{moles } \text{H}_2\text{PO}_4^-)} = \frac{(7.5 \times 10^{-3})(0.046)}{(0.025)} = 1.38 \times 10^{-2} \text{ M}$$

So, after the addition of HCl, the new pH will be  $-\log(2.01 \times 10^{-2}) = 1.86$ . The expected change in pH will be  $1.86 - 2.50 = -0.64$  pH units.

### **Additional Questions** (for the finished lab report)

- For each of these desired pH values, choose a weak acid-conjugate base pair from your textbook that could be used to prepare a buffer solution with that pH. Calculate the desired  $[A^-]/[HA]$  ratio in each case.
  - pH = 6.00
  - pH = 8.00
  - pH = 11.00
- 500 mL of a buffer solution contains 0.050 mol  $\text{NaHSO}_3$  and 0.031 mol  $\text{Na}_2\text{SO}_3$ .
  - What is the pH of the solution?
  - Write the net ionic equation for the reaction that occurs when NaOH is added to this buffer.
  - Calculate the new pH after 10. mL of 1.0 M NaOH is added to the buffer solution.
  - Calculate the new pH after 10. mL of 1.0 M NaOH is added to 500. mL of pure water.
  - Explain why the pH of the water changed so much as compared to the pH of the buffer.