AP Lab #19 –
Preparation and Properties of Buffer Solutions

Lab Objectives

- Acids and bases
- Buffers
- Chemical equilibrium
- LeChâtelier's principle
- Titrations

Overview

In this lab, a number of buffer solutions will be studied by applying various experimental techniques. The response of these buffers to the addition of acid and base will be determined. The pH of these stressed buffers will then be compared with the calculated values from the Henderson-Hasselbalch equation.

Background

The function of a buffer is to resist a change in the pH of a system. A buffer usually consists of a weak acid and its conjugate base or a weak base and its conjugate acid. Buffers may also be prepared by neutralizing some of the weak acid solution with a strong base, or neutralizing some of the weak base with a strong acid solution. In addition, many commercial buffers are prepared by mixing weak acids with weak bases such as borax and citric acid. Unfortunately, buffers are only effective within ±1 pH unit of the acid's pK_a.

How do buffers work? A buffer is usually a mixture of a weak acid and its conjugate base at equilibrium. Buffers are an excellent application of LeChâtelier's principle. LeChâtelier's principle states that changing the amount of one species in the system will cause the other substances in the system to react, relieving the stress.

$$HA(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + A^-(aq)$$

HA = Un-ionized acid
H_3O^+ = Hydronium ions in solution
A^- = Conjugate base in solution

In this example, if an additional source of acid were added, the equilibrium would be pushed toward the un-ionized acid and water. Note that water will *not* affect the equilibrium, as it dilutes all species equally.

This concept can be extended to the idea of the equilibrium constant, K_a. The equilibrium constant for a weak acid is given as follows:

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

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Background (continued)

Just as the concentration of hydronium, $[H_3O^+]$, can be converted to pH by taking its negative logarithm, K_a can be converted to pK_a by taking its negative logarithm.

$$pH = -\log [H_3O^+]$$
$$pK_a = -\log K_a$$

These formulas can be combined into one which describes the interaction of a weak base and its conjugate acid.

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

This form of the equilibrium expression is known as the Henderson-Hasselbalch equation. The Henderson-Hasselbalch equation in this form can be used to calculate the amount of the weak acid and its conjugate base that must be combined to prepare a buffer solution with a specific pH value.

Sample Calculation

1. One method of preparing a buffer solution is by mixing measured volumes of weak acids and their conjugate base. Calculate the pH of a solution consisting of a mixture of 50 mL of 0.090 M formic acid, HCOOH(aq), and 50 mL of 0.160 M sodium formate solution, NaHCOO(aq). (The K_a of HCOOH is 1.77×10^{-4}.)

   Concentrations of solutions must be re-calculated when they are combined, due to dilution.

   $V_2 = 100$ mL

   $$M_1V_1 = M_2V_2 \text{ or } M_2 = \frac{M_1V_1}{V_2}$$

   $$[\text{formic acid}] = \frac{(50\text{ mL})(0.090\text{M})}{(100\text{ mL})} = 0.045\text{ M}$$

   $$[\text{sodium formate}] = \frac{(50\text{ mL})(0.160\text{ M})}{(100\text{ mL})} = 0.080\text{ M}$$

   $$pK_a = -\log(K_a) = -\log(1.77 \times 10^{-4}) = 3.75$$

   $$pH = 3.75 + \log \frac{[NaHCOO]}{[HCOOH]}$$

   $$= 3.75 + \log \frac{0.080\text{ M NaHCOO}}{0.045\text{ M HCOOH}} = 3.75 + 0.25 = 4.00$$

Sample Calculation (continued)

2. A variation of this topic would be to prepare buffers starting with pure solids or liquids.

   For example, determine the mass of anhydrous sodium carbonate, Na_2CO_3, which must be added to 100. mL of 0.100 M sodium bicarbonate solution, $NaHCO_3(aq)$, to give a solution with a pH of 11.00. The K_a of $NaHCO_3$ is 5.6×10^{-11}.

   $pK_a = -\log(K_a) = -\log(5.6 \times 10^{-11}) = 10.25$

   # moles(mmol) = volume(mL) × molarity(mol/L)

   # moles of $NaHCO_3$ = 100. mL × 0.1 M = 10.0 mmol $NaHCO_3$

   $$11.00 = 10.25 + \log \frac{x \text{ mol } Na_2CO_3}{10.0 \text{ mol } NaHCO_3};$$

   $$11.00 - 10.25 = \log \frac{x \text{ mol } Na_2CO_3}{10.0 \text{ mol } NaHCO_3} = 0.75$$

   $$\text{inverse log}\left[0.75 = \log \frac{x \text{ mmol } Na_2CO_3}{10.0 \text{ mmol } NaHCO_3}\right]$$

   $$10^{0.075} = \frac{x \text{ mmol } Na_2CO_3}{10.0 \text{ mmol } NaHCO_3} = 5.6$$

   $5.6 \times 10.0 \text{ mmol } Na_2CO_3 = x \text{ mmol } Na_2CO_3$

   # mmol Na_2CO_3 = 56 mmol = 0.056 mol Na_2CO_3

   mass Na_2CO_3 = 0.056 mol × 106 g/mol = 5.9 grams Na_2CO_3

3. Another variation of this type of problem is to add acid or base to a buffer mixture. *Note:* In this variation, moles can be used in place of concentration because the final volume contains both the acid and the base.

   (a) If 50 mL of 0.20 M oxalic acid, $H_2C_2O_4$, is mixed with 400 mL of 0.20 M potassium hydrogen oxalate, KHC_2O_4, what is the pH of the mixture? The K_a of oxalic acid is 6.46×10^{-2}.

   $pK_a = -\log(K_a) = -\log(6.46 \times 10^{-2}) = 1.19$

   # moles(mmol) $H_2C_2O_4$ =
   50.0 mL × 0.40 M = 20. mmol $H_2C_2O_4$

   # moles(mmol) KHC_2O_4 =
   400. mL × 0.20 M = 80. mmol KHC_2O_4

   $$pH = pK_a + \log \frac{\text{moles of } KHC_2O_4}{\text{moles of } H_2C_2O_4}$$

   $$= 1.19 + \log \frac{80.0 \text{ mmol } KHC_2O_4}{20.0 \text{ mmol } H_2C_2O_4} = 1.19 + 0.60 = 1.79$$

Sample Calculation (continued)

(b) If 50.0 mL of 0.10 M HCl is then added to the $H_2C_2O_4/KHC_2O_4$ mixture in Sample Calculation 3(a), what is the pH of the mixture?

When 50.0 mL of 0.10 M HCl or 5.0 mmol (50.0 mL × 0.10 M) is added to the oxalic acid/potassium hydrogen oxalate buffer, the added acid reacts stoichiometrically with the base, KHC_2O_4, producing additional oxalic acid, forcing the pH down from the original 1.79 to 1.67.

	$HC_2O_4^-$(aq)	+	H^+(aq)	→	$H_2C_2O_4$(aq)
I – Initial	80 mmol		5 mmol		20 mmol
C – Change	– 5.0 mmol		– 5.0 mmol		+ 5.0 mmol
E – Equilibrium	75 mmol		0 mmol		25 mmol

Substituting in the new values for the number of moles of oxalic acid and potassium oxalate in the Henderson-Hasselbalch equation will give a new pH of the mixture.

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{\text{moles of } KHC_2O_4}{\text{moles of } H_2C_2O_4}$$

$$= 1.19 + \log \frac{75 \text{ mmol } KHC_2O_4}{25 \text{ mmol } H_2C_2O_4} = 1.19 + 0.48 = 1.67$$

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Pre-Lab Questions

Buffer Solutions

Answering the following questions will help prepare for the concepts covered in this lab.

1. Write balanced chemical equations for the dissolution of acetic acid (CH_3COOH) and sodium acetate ($NaCH_3COO$) in water.

2. Write the Henderson-Hasselbalch equation for a buffer solution of acetic acid and sodium acetate.

3. What would be the pH of a buffer solution prepared by mixing equal volumes of 0.20 M acetic acid and 0.20 M sodium acetate solutions? The K_a of acetic acid is 1.76×10^{-5}.

4. What is the ratio of the acetate ion concentration to acetic acid concentration in an acetic acid/sodium acetate buffer with a pH of 5.00?

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Pre-Lab Questions **(continued)** **Buffer Solutions**

5. Use the Henderson-Hasselbalch equation to calculate the mass of sodium acetate, $NaCH_3COO$, that must be mixed with 30.0 mL of 1.0 M acetic acid to prepare a pH 4 buffer. Record the mass here, and in the space provided on the data sheet on pg S10.

AP Lab #19 – Buffer Solutions

Materials

Chemicals

- Acetic acid solution, CH_3COOH, 0.2 M, 15 mL
- Acetic acid solution, CH_3COOH, 1.0 M, 50 mL
- DI water, 60 mL
- Hydrochloric acid solution, HCl, 0.1 M, 50 mL
- Sodium acetate solution, $NaCH_3COO$, 0.2 M, 15 mL
- Sodium acetate solution, $NaCH_3COO$, 1.0 M, 15 mL
- Sodium acetate, $NaCH_3COO$, 0.5–1.0 g
- Sodium hydroxide solution, NaOH, 0.1 M, 50 mL

Lab Supplies and Equipment

- Beaker, 50-mL, 2–6
- Graduated cylinder, 10-mL
- Graduated cylinder, 25-mL
- pH meter/probe
- Spatula
- Stir rod, glass
- Wash bottle with DI water
- Magnetic stirrer and stir bar (optional)

Safety ⚠

- Read all instructions thoroughly before you begin.
- Wear safety goggles at all times during this experiment.
- Acetic acid, sodium hydroxide and hydrochloric acid are corrosive to all body tissue, especially skin and eyes, and may cause severe burns. Immediately use running water to wash any areas that come in contact with any of these chemicals. Handle with care, and clean up any spills immediately.
- Sodium hydroxide and hydrochloric acid are toxic by ingestion.
- Sodium acetate is a body tissue irritant. Avoid excessive exposure.
- Follow all classroom safety procedures.
- Wash your hands thoroughly with soap and water before leaving the laboratory.

AP Lab #19 – Buffer Solutions

Setup/Preparation

→ If necessary, calibrate your pH meter as described by the instructor.

→ Have all needed solutions readily available, and graduated cylinders cleaned and at hand.

Procedure

First Buffer

1. Add 15.0 mL of 0.20 M acetic acid, CH_3COOH, to a 50-mL beaker. Record the pH of the solution.
2. Add 15.0 mL of 0.20 M sodium acetate, $NaCH_3COO$, to the acetic acid solution, stir, and record the pH of the mixture.
3. Remove 15.0 mL of the mixture and store it in another clean, dry 50-mL beaker.
4. Dilute both halves of the acetic acid/sodium acetate buffers by adding 15.0 mL of DI water to each. Record the pH of the first solution. Note that both halves will have the same pH.
5. Add 5 mL of 0.1 M hydrochloric acid, HCl(aq), to the diluted acetic acid/sodium acetate buffer solution. Record the pH of the solution.
6. Add another 5-mL portion of 0.1 M HCl to the same beaker and record the pH of the solution.
7. Add 5 mL of 0.1 M sodium hydroxide, NaOH(aq), to the acetic acid/sodium acetate buffer solution in the second beaker. Record the pH.
8. Add another 5-mL portion of 0.1 M NaOH to the second beaker. Record the pH.
9. Dispose of all solutions as described by the instructor.

Second Buffer

1. Clean and dry two 50-mL beakers. Measure 15.0 mL of 1.0 M acetic acid into one of the beakers and record the pH.
2. Add 15.0 mL of 1.0 M sodium acetate to the 1.0 M acetic acid solution, stir, and record the pH.
3. Remove 15.0 mL of the mixture, storing it in another clean, dry 50-mL beaker.
4. Dilute both halves of the acetic acid/sodium acetate buffers by adding 15.0 mL of DI water to each beaker. Record the pH of the first solution. Note that both halves will have the same pH.

Procedure Tips

→ Record all data immediately in the data table on page S10.

→ Be certain that the following procedures are completed between each step in this experiment.

- *Thoroughly rinse the pH electrode with DI water between trials.*
- *Stir or swirl the solution thoroughly after each addition, preferably for at least 30 seconds.*
- *Measure the pH of each mixture, recording the value in the space provided on the data table.*
- *Read the concentrations in the procedure carefully.*

Procedure (continued)

5. Add 5 mL of 0.1 M hydrochloric acid, HCl(aq), to the diluted 1.0 M acetic acid/1.0 M sodium acetate buffer solution. Record the pH of the solution.
6. Repeat the process of adding 5-mL portions of 0.1 M HCl to the same buffer solution until a total of 25 mL of hydrochloric acid has been added. Record the pH after each addition.
7. Add 5 mL of 0.1 M sodium hydroxide, NaOH(aq), to the 1.0 M acetic acid/1.0 M sodium acetate buffer solution in the second beaker. Record the pH.
8. Repeat the process of adding 0.1 M NaOH in 5-mL portions to the same buffer solution until a total of 25 mL of sodium hydroxide has been added. Record the pH after each addition.
9. Dispose of all solutions as described by the instructor.

Third Buffer

1. Clean and dry a 50-mL beaker.
2. Tare the beaker and add the mass of anhydrous sodium acetate, $NaCH_3COO$, calculated in the Pre-Lab Question 5. Based on the precision of the balance, record the actual mass added, at the bottom of the data table.
3. Add 30.0 mL of 1.0 M acetic acid and stir or swirl to dissolve the sodium acetate. Record the pH on the data table.
4. Dispose of all solutions as described by the instructor.

Disposal and Cleanup

- Dispose of all chemicals and solutions as instructed by your teacher.
- Clean all glassware and return all equipment and supplies to their proper place.
- Rinse the pH electrode and store it according to your teacher's instructions.
- Wash your hands thoroughly before leaving the laboratory.

Name ____________________

Data Table

Buffer Solutions

Step	Contents of the Beaker	Measured pH	Calculated pH
First Buffer			*First Buffer*
1	15.0 mL of 0.20 M CH_3COOH		
2	Added 15.0 mL of 0.20 M $NaCH_3COO$		
4	Divide, then add 15.0 mL DI water		
5	Add 5 mL 0.1 M HCl		
6	Add a second portion of 5 mL of 0.1 M HCl		
7	Add 5 mL 0.1 M NaOH to the second half of the mixture prepared in step 2		
8	Add a second portion of 5 mL of 0.1 M NaOH		
Second Buffer			*Second Buffer*
1	15.0 mL of 1.0 M CH_3COOH		
2	Added 15.0 mL of 1.0 M $NaCH_3COO$		
4	Divide, then add 15.0 mL DI water		
5 and 6	Add 5 mL of 0.1 M HCl		
	Add a second 5-mL portion of 0.1 M HCl		
	Add a third 5-mL portion of 0.1 M HCl		
	Add a fourth 5-mL portion of 0.1 M HCl		
	Add a fifth 5-mL portion of 0.1 M HCl		
7 and 8	Add 5 mL 0.1 M NaOH to the second half of the mixture prepared in step 2		
	Add a second 5-mL portion of 0.1 M NaOH		
	Add a third 5-mL portion of 0.1 M NaOH		
	Add a fourth 5-mL portion of 0.1 M NaOH		
	Add a fifth 5-mL portion of 0.1 M NaOH		
Third Buffer			*Third Buffer*
3	The buffer solution containing solid sodium acetate in 30.0 mL of 1.0 M acetic acid		

Pre-Lab Question 5: Calculated mass of sodium acetate to be added for third buffer: ____________

Actual Mass of sodium acetate added: ____________

Name ______________________

Questions and Calculations

Buffer Solutions

1. Calculate the expected pH of each solution studied in the first buffer of this experiment. Record the results in the space provided on the data table. Show all calculations. *Hint:* Recall that when equal volumes of two solutions are mixed, their concentrations become one-half the original values. Likewise, watch for other dilutions as they must be considered in the calculations.

- pH of 15 mL of 0.2 M acetic acid

- 15 mL of 0.20 M sodium acetate is added to the acetic acid. *Note:* Each solution is now diluted by one-half.

- 15 mL of the buffer is diluted to 30 mL. Therefore, the concentration is decreased by one-half and is now 0.05 M.

- 5.0 mL of 0.1 M HCl is added to the buffer mixture.

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Questions and Calculations (continued)

- A second 5.0-mL portion of HCl is added to the mixture.

- 5.0 mL of 0.1 M NaOH is added to the second half of the undiluted buffer mixture.

- A second 5.0-mL portion of NaOH is added to the buffer.

2. (a) In Procedures 1 for the first buffer and 1 for the second buffer, the pH of 0.20 M and 1.0 M acetic acid solutions was measured. Using the pH and molar concentrations, calculate the percent ionization for both acetic acid solutions.

   (b) How would you classify acetic acid, as either a weak or strong acid based on the percent ionization? How could the degree of ionization be used to classify acids as strong or weak acids?

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Questions and Calculations (continued)

(c) Calculate the K_a of acetic acid from the pH and molar concentrations using both 0.2 M and 1.0 M acetic acid solutions.

3. Describe how the buffer solution prevents significant pH change when small amounts of HCl and NaOH are added. Use chemical equations as part of your answer.

4. The buffer capacity of a solution is a measure of the amount of acid or base a buffer solution can absorb without undergoing large changes in pH. Which buffer system, 0.2 M acetic acid or 1.0 M acetic acid, had the greatest buffer capacity? Explain your rationale with lab data.

5. Suppose you wanted to increase the buffer capacity of the acetate/acetic acid buffer. What would you do? Explain your answer.