Online Activity 3

Buffer Effects

Introduction

A **buffered solution** is an aqueous solution that contains both a weak acid and its conjugate base. By having both acidic and basic properties, a buffer has the ability to resist changes in pH. **Buffers** are important in biological systems to maintain proper blood chemistry and in the environment to help minimize effects of acid rain. A buffer works by using the equilibrium between the acid and its conjugate base to minimize the effect that the addition of a small amount of additional acid or base has on the pH.

Buffers work chemically by shifting the equilibrium between the weak acid and the conjugate base in the following manner. If a strong acid is added, it uses up some of the conjugate base and produces more of the weak acid. The pH may shift slightly downward due to the small amount of dissociation of the weak acid, but it is much less of a shift than would be seen by adding the strong acid directly to water, where each mole of acid added adds directly to the $[H_3O^+]$.

Strong Acid in water:	$HCl + H_2O \rightarrow H_3O^+ + Cl^-$
Buffer Equilibrium:	$HA + H_2O \leftrightarrows H_3O^+ + A^-$
Buffer Absorption of acid:	$HCl + A- \rightarrow HA + Cl^-$

Since no H_3O^+ is produced directly by the addition of the strong acid, there is minimal shift in pH.

Buffers offer similar protection against changes in pH due to the addition of a strong base. In this case, the weak acid absorbs the base.

Buffer Equilibrium:	$HA + H_2O \leftrightarrows H_3O^+ + A^-$
Buffer Absorption of base:	$HA + OH^- \rightarrow H_2O + A^-$

Thus, in a similar manner to the addition of acid, no explicit change in OH^- or H_3O^+ is seen, so there is minimal change in the pH. The pH is governed only by the equilibrium constant, K_a, not directly by the addition of base or acid as would be seen in a water solution.

$$HA + H_2O \leftrightarrow H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The Henderson-Hasselbalch Equation

There are some restrictions in the preparation of a buffer. Unlike a weak acid equilibrium, where an ICE table is needed to determine the degree of equilibrium concentrations of the weak base, the weak base is added directly to the solution, so the concentrations of HA and A- in the initial line in the ICE table is already accounted for.

	$HA(aq)$	+	H_2O (l)	$\leftrightarrows$	H_3O^+ (aq) +	A^-(aq)
Initial	1.0M				0M	1.0M
Change	-1x				+1x	+1x
Equilibrium	(1.0-1x)				(0+1x)	(1.0+1x)

To fully absorb any strong acid or base that is added, the concentrations of the conjugate acid and base must be high enough that the amount that dissociates, x, is negligible in the equilibrium concentrations of both HA and A^-. A rule of thumb is that you must have the acid and base concentrations at least 100x greater than the K_a for the dissociation to become negligible.

	HA(aq)	+	H_2O (l)	⇆	H_3O^+ (aq) +	A^-(aq)
Initial	1.0M				0M	1.0M
Change	-1x				+1x	+1x
Equilibrium	1.0M				0+1x	1.0M

Once you have satisfied this criteria, then you can use the Henderson-Hasselbalch equation instead of an ICE table to solve buffer problems. This equation uses the same information given in the equilibrium line in the ICE table, but is much quicker, especially when multiple pH calculations must be made. The **Henderson-Hasselbalch equation** is as follows:

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

It is a rearrangement of the K_a expression in terms of pH instead of $[H_3O^+]$ and can be used to very quickly determine the concentration of buffer components needed to provide a particular pH for a system. It can also be used to determine the ratio of the weak acid and its conjugate base from the pH of the solution.

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

$$\mathrm{pKa} = -\log\frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = -\log[\mathrm{H_3O^+}] - \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = \mathrm{pH} - \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

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

Finally, because the ratio of the conjugate base to the acid is constant, there are no changes in pH seen in a buffer when it is diluted, as there is no explicit change in the $[H_3O^+]$. If a small amount of strong acid is added, it removes some of the conjugate base and increases the acid by the same amount. These changes are made in the actual concentrations of HA and A^- in the Henderson-Hasselbalch equation before the recalculation of pH is made. More explicit instructions on working with the Henderson-Hasselbalch equation and ICE tables are given in the calculations section of the lab.

In Your Activity…

In this activity, you will study the pH changes that result when adding small amounts of a strong acid and base to a buffer and directly to an unbuffered (water) solution. You will also learn how to perform the calculations necessary when working with buffers and to calculate the changes in pH that result when the buffer equilibrium is shifted due to the addition of acid and base.

The link to the simulation is: https://pages.uoregon.edu/tgreenbo/pHbuffer20.html

Online Activity 3: Activity Procedures and Data Sheet

Submit as part of your activity report

Name: ____ Date: ________ Section: ________

Record all measurements with units and the maximum number of significant figures provided by the simulation.

The link to the simulation is: https://pages.uoregon.edu/tgreenbo/pHbuffer20.html

Part 1: Addition of a strong acid and base to a buffer solution

1. Select Acetic Acid ($HC_2H_3O_2$) as the acid for your buffer. Set the concentration to 10.00 x 10^{-2} and the volume to 100.00mL.

2. Select Sodium Acetate ($NaC_2H_3O_2$) as the conjugate base for your buffer. Set the concentration to 10.00 x 10^{-2} and the volume to 100.00mL.

3. Click on the pink square with the down arrow to lower the pH probe into your buffer solution.

4. Record the pH of the buffer from the reading on the pH meter.

pH of buffer before the addition of HCl: ____________________

5. Click on the blue up arrow box to raise the pH probe.

6. Click on the orange colored square that says “Go to Part II”.

7. Select Acid from the Test Solutions options box then select HCl as your Acid.

8. Leave the amount of moles set at 1.00x10^{-3} mole.

9. Click the pink down arrow box to lower the pH probe into the solution.

10. Record the pH of the buffer from the reading on the pH meter.

pH of buffer after the addition of HCl: ____________________

11. Click on the blue up arrow box to raise the pH probe.

12. Select base in the Test Solutions box.

13. Choose NaOH as your base. Leave the amount of moles set to 1.00x10^{-3} moles.

14. Click the pink down arrow box to lower the pH probe into the solution,

15. Record the pH of the buffer from the reading on the pH meter.

pH of buffer after the addition of NaOH: ____________________*
*the NaOH is being added to fresh buffer, not buffer containing HCl

16. Click on the blue up arrow to raise the pH probe.

17. Click on the orange square that says “Go to Part 1”

Part 2: Addition of a strong acid & base to water

1. Since the simulation does not provide a distilled water version, this information is being provided to you. Note that distilled water can be somewhat acidic as a result of carbonic acid from dissolved CO_2.

pH of 15.0 mL water without added acid or base: __5.33________________

pH of water after the addition of 1.0 mL of 0.10M HCl: __2.20_____________

pH of water after the addition of 1.0mL of 0.1M NaOH: __11.25______________

Grading

Points

Neatness and Clarity of Data	5pts	__________pts
Significant figures and units	5pts	__________pts
All data is present	10pts	__________pts

Deductions (sliding based on TA discretion)

Lab area left unclean	20pts	__________pts
Improper waste disposal	20pts	__________pts
Disruptive behavior	20pts	__________pts
Other: ____		__________pts

Plagiarism!!! Data are identical to another student 100pts _________pts

Grade for Experimental Procedures and Data ________pts

Experiment 6: Results Table

Submit as part of your activity report

Name: ____ Date: ________ Section: ________

Record all results with the correct number of significant figures and units

Table 1: Weak acid/weak base buffer calculations

Concentration of the acetic acid in the buffer solution	
Concentration of the acetate ion in the buffer solution	
Theoretical pH of the buffer solution before the addition of acid or base	
Equilibrium concentration of acetic acid after the addition of HCl	
Equilibrium concentrations of acetate Ion after the addition of HCl	
Equilibrium concentration of acetic acid after the addition of NaOH	
Equilibrium concentrations of acetate Ion after the addition of NaOH	
Theoretical pH of the buffer solution after the addition of HCl	
Theoretical pH of the buffer solution after the addition of NaOH	

Table 2: Strong acid/strong base calculations

Concentration of Diluted HCl	
Concentration of Diluted NaOH	
Concentration of the $[H_3O^+]$ in the water after the addition of HCl	
Concentration of the $[H_3O^+]$ in the water after the addition of NaOH	
Theoretical pH of the Water Solution after the addition of HCl	
Theoretical pH of the Water Solution after the Addition of NaOH	

Grading

<u>Points</u>

Significant figures and units	5pts	__________pts
Table is neat and legible	5pts	__________pts
All results are present	10pts	__________pts

<u>Deductions (sliding based on TA discretion)</u>

Results do not make sense	20pts	__________pts
Results do not match data	20pts	__________pts
Other: ____		__________pts

Plagiarism!!! Results are identical to another student 100pts __________pts

Grade on results table __________pts

Calculations Section

Submit as part of your activity report

Calculating the Molarity of the Acetic Acid and Acetate Ion in the Buffer Solution

The dilution was made by using 100.0 mL each of acetic acid and sodium acetate. The variable, M_1, in the equation corresponds to the concentration of the stock solution of acetic acid or sodium acetate (both were 0.1000 M). Use the following equation and solve for the diluted molarity for the acetic acid, M_2 acetic acid. Then repeat the calculation for the sodium acetate, M_2, sodium acetate.

$$M_1V_1=M_2V_2$$

Concentration of the Acetic Acid in the Buffer Solution ____________________

Concentration of the Acetate Ion in the Buffer Solution ____________________

Theoretical pH of the Buffer Solution before the Addition of HCl or NaOH

Use the Henderson-Hasselbalch equation to calculate the pH of the buffer solution. This equation can be used as long as the amount of dissociation of the acid to $[H_3O^+]$ is considered negligible as it was for the buffer solutions in this experiment.

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = -\log(1.8\mathrm{x}10^{-5}) + \log\frac{[\mathrm{M_2acetate\ ion}]}{[\mathrm{M_2acetic\ acid}]}$$

Theoretical pH of the Buffer Solution before the Addition of Acid or Base ____________________

Equilibrium Concentrations of Acetic Acid and Acetate Ion after the addition of HCl

Each mole of HCl added to the buffer solution uses up 1 mole of the acetate ion and produces 1 mole of acetic acid. Calculate the equilibrium values of the acid and base as shown below.

$1HCl + 1\ C_2H_3O_2^- \rightarrow 1Cl^- + HC_2H_3O_2$

For each mole of HCl added: 1 mole less acetate 1 mole acetic acid produced

(Initial moles of $HC_2H_3O_2$ + moles of HCl) / Volume of solution in L = Equilibrium concentration of $HC_2H_3O_2$

(Initial moles of $C_2H_3O_2^-$ - Moles of HCl) / Volume of solution in L = Equilibrium concentration of $C_2H_3O_2^-$

Equilibrium concentration of acetic acid in the buffer solution with 0.00100 moles HCl ________________

Equilibrium concentration of acetate ion in the buffer solution with 0.00100 moles HCl ________________

Equilibrium Concentrations of Acetic Acid and Acetate Ion after the addition of NaOH

Each mole of NaOH added to the buffer solution uses up 1 mole of the acetic acid and produces 1 mole of acetate ion. Calculate the equilibrium values of the acid and base as shown below.

$NaOH + HC_2H_3O_2 \rightarrow H_2O + C_2H_3O_2-$

For each mole of NaOH added: 1 mole less acetic acid 1 mole acetate produced

(Initial moles of $HC_2H_3O_2$ - moles of NaOH) / Volume of solution in L = Equilibrium conc. of $HC_2H_3O_2$

(Initial moles of $C_2H_3O_2^-$ + moles of NaOH) / Volume of solution in L = Equilibrium conc. of $C_2H_3O_2^-$

Equilibrium concentration of acetic acid in the buffer solution with 0.00100 moles NaOH ________________

Equilibrium concentration of acetate ion in the buffer solution with 0.00100 moles NaOH ________________

Theoretical pH of the Buffer Solution after the Addition of Acid or Base

Use the Henderson-Hasselbalch equation to calculate the pH of the buffer solution after the addition of HCl and NaOH by substituting the equilibrium values of acetic acid and acetate ion calculated in the previous sections. The pH should decrease slightly to account for the addition of the HCl and increase slightly for the addition of the NaOH when compared to the pH of the original buffer.

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = -\log(1.8\mathrm{x}10^{-5}) + \log\frac{[\mathrm{M_2\ acetate}]}{[\mathrm{M_2 acetic\ acid}]}$$

pH of the buffer solution after adding 1mL of HCl ____________________

pH of the buffer solution after adding 1mL of NaOH ____________________

Concentration of Diluted HCl or NaOH in the Water

The addition of 1 mL of HCl or NaOH to the water increases the total volume of the solution and dilutes the concentration of the HCl or NaOH added. Use the equation, $M_1V_1=M_2V_2$ to find the concentrations of the diluted HCl and NaOH solutions.

M_1 is the molarity of the HCl or NaOH from the stock solution.
V_1 is 1.0 mL: volume of the HCl or NaOH solution
V_2 is 16.0 mL: total volume of the solution = 15.0 mL water + 1 ml HCl or NaOH
Solve for M_2, the molarity of the diluted HCl or NaOH

Concentration of diluted HCl solution ____________________

Concentration of diluted NaOH solution ____________________

Theoretical Concentration of [H_3O^+] for diluted HCl

Strong acids fully dissociate in water, so the molarity of the [H_3O^+] in the diluted solution is equal to the concentration of the diluted HCl solution.

Theoretical concentration of [H_3O^+] for diluted HCl ____________________

Theoretical Concentration of [H_3O^+] for NaOH in Water

Strong bases fully dissociate in water, so the molarity of the [OH^-] in the water after the dilution is the same as the diluted concentration of the NaOH. The [H_3O^+] in the diluted solutions is related to the [OH^-] in the water through the K_w. Rearrange the following equation below to calculate the [H_3O^+] from the concentration of the diluted NaOH solution and the K_w.

$$K_w = 1x10^{-14} = [H_3O^+][OH^-]$$

Theoretical concentration of [H_3O^+] for diluted NaOH ____________________

Theoretical pH for HCl or NaOH in Water

Find the theoretical pH of the water solutions with added acid or base using the following equation.

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

pH of diluted HCl ____________________

pH of diluted NaOH ____________________

Questions:

Submit as part of your online activity report

Record all values with the correct number of significant figures and units.
Place all numerical answers on the line next to the question.
Show calculations for any numerical answers.

1. Briefly explain how buffers are able to prevent significant changes in pH when:
   a. A strong acid is added

   b. A strong base is added

Answer Question 2 using this data:
For 1.0L of an acetic acid solution: $K_a = 1.8 \times 10^{-5}$ and [HA] = 0.250M

2. A. Calculate the pH of the solution.

   ____

   B. What is the pK_a?

   ____

   C. Calculate the pH of the solution if you make it a buffer by adding enough solid sodium acetate to make the concentration of acetate ion equal to 0.35M. The volume of the solution does not change.

   ____

   D. What is the new concentration of [HA] if 2.0mL of 5.00M of HCl is added to 1.000L of the solution above? Note that there is a volume change here.

   ____

   E. What is the new pH?

   ____

3. A. Give an example of a sodium salt that would be a conjugate base for a buffer solution containing the weak acid HCN.

   ____

   B. Write the chemical equation associated with this weak base dissociating in water.

   ____

   C. Write the K_b expression for this reaction.

   ____

   D. Calculate the pH of a 1.0M solution of this salt. K_a= 6.2×10^{-10} for HCN.

   ____