

Experiment 32

BUFFERS¹

1/13/2020

MATERIALS: Small plastic vials (12), 10 mL pipets (2), pipet bulbs (2), 50 mL buret, 50 mL volumetric flask, stirring rods (2), plastic beakers (10), plastic droppers (6), weighing boats (2), straw, pH meter.

PURPOSE: The purpose of this experiment is to develop the concept and study the properties of buffers.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Distinguish between strong acid and weak acid systems.
2. Define a buffer and explain how a buffer works.
3. Explain how an acid-base indicator is used in the laboratory.
4. Qualitatively describe the important regions of a titration curve.
5. Prepare a buffer at a specified pH.
6. Calculate the change in pH of a simple buffer solution of known composition caused by adding a small amount of strong acid or strong base.

PRE-LAB: Complete the Pre-Lab Assignment at the end of this document before going to lab. You will need some of the answers to these questions in order to get started with the experiment.

DISCUSSION:

The basis for the Brønsted/Lowry acid/base model is proton (**hydrogen ion, H⁺**) transfer. The species that starts with the proton and loses it is called an **acid** or **proton donor**, and, the other side of the transfer is the species that gets the proton, and it is called a **proton acceptor** or **base**. As shown in Figure 1, the bond to the proton in the acid is broken while the bond to the proton in the base is made. One can think of it as the proton leaves behind one lone-pair and makes a bond using another.

Acids and Bases: What are they and how do they behave

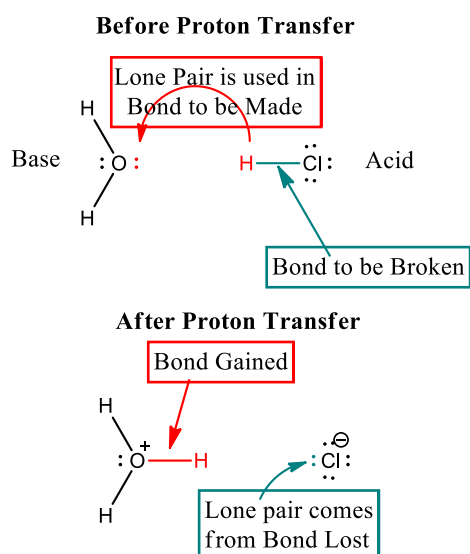


FIGURE 2: BRØNSTED/ LOWRY REACTION OF STRONG ACID, HCL, WITH WATER.

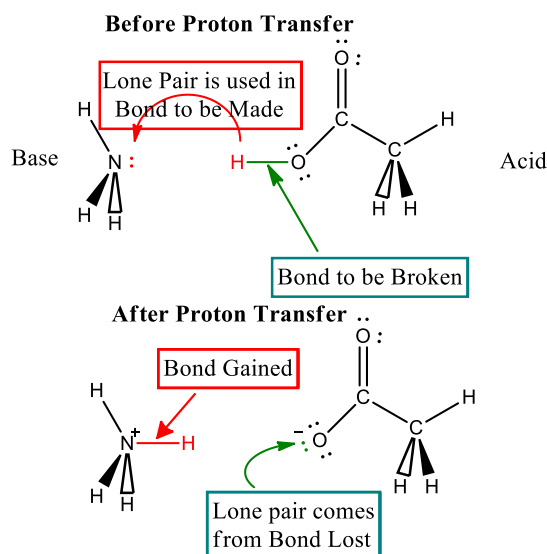


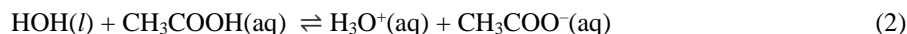
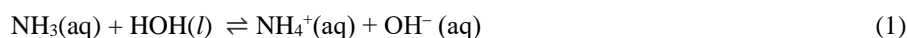
FIGURE 2: BRØNSTED/ LOWRY REACTION OF WEAK BASE, AMMONIA, WITH WEAK ACID, ACETIC ACID.

¹Partially adapted from "Working with Chemistry, A Laboratory Inquiry Program" by Wink, S.F. Gislason, and J.E. Kuehn, W.H. Freeman and Company, 2000.

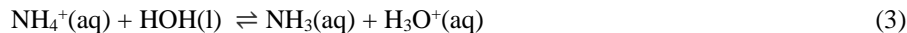
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Potentially, any molecule or ion with a hydrogen can be an acid, and any molecule or ion with a lone-pair can be a base. However, in practice the hydrogen in a neutral acid needs to be bound to an electronegative atom like a Group 16 or 17 atom, such as O or F. The Group 15 atom, such as N or P, in a neutral compound will have three bonds and a lone-pair and will often make a good base. Another proton transfer (acid/base) reaction is given in Figure 2 the hydrogen bound to the oxygen of acetic acid with the lone-pair of nitrogen in ammonia (Figure 2).

Note that in Figure 2, after the transfer, the nitrogen on the ammonium ion has both hydrogen and a positive charge, and oxygen on the acetate ion has a negative charge. One might ask why the proton does not transfer back to the original configuration, and as it turns out it does. In fact, similar reversible reactions happen with water and either ammonia or acetic acid as illustrated in the equilibria in Reactions 1 and 2.



Water can participate in proton transfer as both a donor (Reaction 1) and an acceptor (Reaction 2). Also, the product of Reaction 1, the ammonium ion, $\text{NH}_4^+(\text{aq})$, can behave as an acid, and the product of Reaction 2, the acetate ion, $\text{CH}_3\text{COO}^-(\text{aq})$, can behave as a base when put into water as part of their respective ionic compounds (Reactions 3 and 4, net ionic reactions without spectator ions, e.g. Cl^- in Reaction 3 and Na^+ in Reaction 4).



A. Acids and Bases: Ranking their strength

All four reactions above go only to partial completion and exist in water as equilibria. We find that the ability of these molecules and ions to hold onto a proton in an equilibrium, its base strength, can be ranked as:



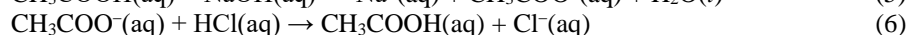
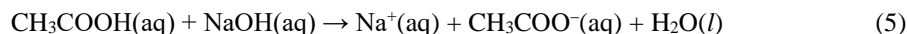
And among the proton donors, the acid strength can be ranked as:



The hydroxide ion (OH^-) is the strongest base that can exist in water and the hydronium ion (H_3O^+), the protonated water, is the strongest acid. So, when a soluble hydroxide such as NaOH is placed in water, the ionic compound dissolves and hydroxide ion is in solution. When an acid that is stronger than water, such as hydrochloric acid as seen in Figure 1, is put into water, it dissociates completely. However, when weak acids and weak bases, such as found in the middle of the two inequalities above, are placed in water they establish an equilibria as illustrated above. Thus we observe that the ability for a weakly acidic compound to donate a proton is somewhere between that of water and the hydronium ion, and the ability for a weakly basic compound to accept a proton is somewhere between that of water and the hydroxide ion.

B. Weak Acids and their Conjugates Coexisting: A Buffer

Because both the weak acid and its conjugate base (e.g., $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ or $\text{NH}_4^+/\text{NH}_3$) can coexist with water, the weak acid/base conjugate pair can coexist with each other in water. When there is a significant amount of both (with between the ratios of 10:1 acid:base or base:acid), this gives rise to a curiously useful situation. We have a solution with both plenty of a) a weak acid that can potentially donate protons to a strong base and b) a weak base that can accept protons from a strong acid, illustrated in Reactions 5) and 6).



This situation is called a Buffer. The acid can act as a source of protons, and the conjugate base can act as a sink for protons.

A Buffer: A Description

A buffer is described by three parameters:

- 1) The combined number of moles of the weak acid and its conjugate base.

The larger the amount (moles) of weak acid, the more of a strong base can react with it, and correspondingly, the larger the amount (moles) of weak base, the more of a strong acid can react with it. Thus, the higher the concentrations of weak acid and conjugate base, the stronger the buffer, i.e., the more resistant it is to pH change upon addition of strong acid or strong base.

- 2) The strength of the weak acid.

Rather than the loose comparison of acid/base strengths given in the inequalities above, a tighter comparison and a numerical value for acidity can be obtained by determining concentrations of all species for equilibrium solutions such as for the ammonium ion and acetic acid, as in reactions (3) and (4), respectively. With these concentrations, the constant for these equilibria, the Acid Dissociation Constant (K_a) can be determined. The larger the K_a , the more acidic the compound, and thus the easier it is for the acid to lose a proton. Any buffer made will have a $[H_3O^+]$ that is $\frac{1}{10}$ - 10 times the K_a , and thus a $pH \pm 1$ of the pK_a .

- 3) The ratio between [conjugate acid]/[conjugate base]

The conjugate base in a buffer is a place for protons to bind. The lack of a proton on a base is not “nothing”, but the potential for a reaction. So, as we combine weak acid and its conjugate base, we combine *places with protons* that can be donated (acid) and *places where protons can go* (base). When the ratio between acid and base forms of a weak acid/base pair is above 1, then there are more protons to donate than places for protons to go. With this fine tuning, we can use the K_a expression and the definition of pH (and analogously pK_a) to obtain the **Henderson-Hasselbach Equation** defined as Equation 7:

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \quad (7)$$

A curiosity of history and electronics make the most commonly used parameter of hydrogen concentration, pH, decrease logarithmically with increasing $[H_3O^+]$. One consequence is that in deriving the above equation, the ratio is $[base]/[acid]$, that is [empty of protons]/[filled with protons]. This will be useful to the following analogy because empty things are typically above full.

A Buffer: A Reservoir Analogy

Here we will build a reservoir analogy to help comprehend the workings of a buffer. A reservoir is a structure to hold (i.e., reserve) water for future use. A lake behind a dam or a water tower would be two examples. A reservoir is defined by its capacity, useful range and fill-factor. These three parameters are directly analogous to the three given above for a buffer, except a buffer holds protons, not water.

A. Capacity

In developing our analogy, we imagine a water tower as our reservoir because its size and height are obvious, even though the level it is filled to is less obvious than a lake reservoir. The water tower capacity is set, just like a buffer. It can only be filled so far before it overflows and emptied so much before it is drained. It is the same with a buffer; only so many moles of strong acid can be added before it “overflows” with protons, and it has so many protons to be “emptied” by reaction of strong base.

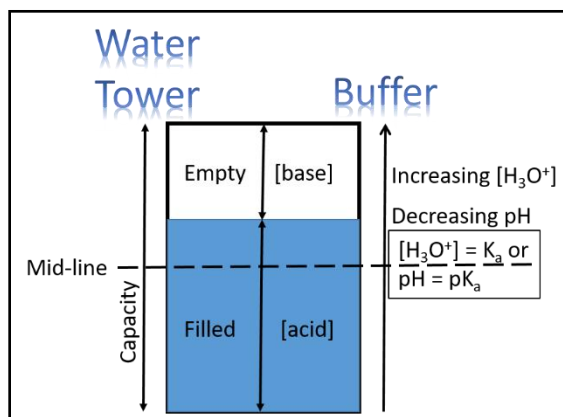


Figure 3: Water Tower analogy of a Buffer. The three factors, 1) Capacity, 2) Mid-line and 3) Fill Factor define both.

	Capacity	Useful Range	Fill Factor
Weak Acid/Base Buffer	Moles acid + moles base	$\frac{1}{10} * K_a < H_3O^+ < 10 * K_a$ or $\log(K_a) \pm 1$	[base]/[acid]
Water Tower	Water Tower volume (empty + full = Capacity)	From nearly the bottom to nearly the top of the tower	Empty:Full ratio

Table 1: Factors in the Buffer-Water Tower Analogy.

B. Useful Range

Gravitational potential (height of the tank) is a common analogy tool for energetics and thermodynamics. Just as the ultimate water pressure of a system is mostly determined by the height of the tower above the user², so the “proton pressure” of a reaction is mostly determined by how acidic the acid is. The altitude of the Mid-line of the water tower (see Figure 3) is inherent to the structure, and the difference in altitude to the user can give a useful estimate of the ultimate water pressure. (Note: For purposes of our analogy, we are going to have to assume that all users are at the same level.)

C. Fill Factor

People, in general, are less concerned with the fine points of the pressure of the water coming out of their taps than that *there should be* water coming out of their taps. Analogously, people, in general are less concerned with the precise pH of a buffer and more concerned that the buffer keeps the pH within an allowed range. So to continue the water tank analogy, as long as the tank has some water (but not overflowing) and is delivering it with sufficient pressure, though certainly the differences in pressure can be measured, no one much cares whether the pressure is a little higher or lower. Biological systems can be exquisitely sensitive to changes in pH, so our analogy breaks down a little in these cases. Knowing and predicting the precise pH is very important, and so the adjustment of pH by changes in [base]/[acid] ratio is subtle, yet important.

Finally, changes in the proton Fill-Factor of buffers are a challenge to calculate. Typically, the Capacity (moles acid + moles base) is fixed, and a strong acid or strong base is added to shift the Fill Factor. The strong acid both increases the weak acid and decreases the conjugate base (strong acid addition) while the strong base does the reverse. If you keep in mind the water tank analogy, the change in concentration of the acid *must equal* the negative of the change of concentration of the base, just as you amount you fill the tank *must equal* the negative of the amount you reduce the empty portion.

The Lab: Measurement and Challenge

In the first week of this lab, you will explore how the acid/base character (measured as pH) changes as you add your breath to pure water. Then you will add a strong acid, strong base and a combination of the two to water. The latter you will find that this is analogous to water without a reservoir. In the next part, you will calculate then observe the pH of solutions, including buffer solutions of different types and concentrations. Then you will stress them with strong acid (HCl) and strong base (NaOH). Following the Reservoir Analogy will help you rationalize the changes wrought by these stresses.

The second week will challenge you to create and adjust buffers. Properly setting the level of your proton reservoir will be a conceptual and mathematical challenge. Keep in mind the direction of change as you add strong acid and strong base. Most of all realize that adding strong acid protonates the weak base. This increases the amount of weak acid (fills the tank) BY REDUCING the amount of conjugate weak base (reducing how much the tank is empty). As you add strong acid (or base), both numerator and denominator in the last term of the Henderson-Hasselbach equation change.

² The typical municipal water supply should be at between 50-100 psi (pounds per square inch) (<https://people.howstuffworks.com/water.htm>). For each foot, water supplies 0.4278 psi. That would mean the water supply should be 117-234 feet above the user. A typical tower is placed on a hill which gives some height, and the tower itself provides the remaining height.

LAB DAY 1:

Note: During the lab period, you will need to reuse your glassware. Don't contaminate your solutions. Acids will be neutralized by even trace amounts of base. **Rinse your glassware thoroughly with distilled water before each use.**

Work with a partner for this part:

1. From your instructor, learn the proper procedures for calibrating the pH meter and obtaining a pH measurement. Record the procedure for future reference.

Procedure for calibrating the pH meter:

2. Obtain a sample of distilled, degassed water from your instructor. Write down the expected pH of the water. Measure the pH. The pH may not completely stabilize so report the value after waiting 1-2 minutes. Is the pH what you expected? Using a clean straw, blow *into* the water for a few minutes and observe the pH (keep the pH electrode in the water). Explain what happened and why.

Distilled, degassed water: Expected pH at 25°C: _____ Measured pH: _____

Effect of bubbling into the water:

Explanation for pH change:

3. Fill a clean 50 mL buret with distilled water. Make sure no air bubbles are trapped in the tip of the buret.

Whenever you need to add 10 mL of distilled water, use this buret to deliver the specified amount.

4. a. With a clean pipet, carefully transfer 10 mL of 0.20 M HCl into a clean plastic beaker. From your buret, add 10 mL of distilled water to the beaker. Mix the solution. What is the concentration of H^+ in this diluted solution? Calculate the expected pH of this solution. Add 3 drops of universal indicator to the solution, mix, and note the color. Measure the pH using a pH meter. Record your data in the table.

b. Repeat the procedure in **part 4a** using 0.20 M NaOH (instead of 0.20 M HCl). Remember to rinse your pipet and stirring rod.

c. Carefully pipet 10 mL of 0.20 M HCl and 10 mL of 0.20 M NaOH into a beaker and mix. Rinse the pipet between solutions. What is the expected pH of this solution? Add 3 drops of universal indicator, mix, and note the color. Measure the pH, then separate the solution equally into 2 vials (10 mL each). Use the graduations on the beaker and the levels of the liquids in the vials to ensure equal volumes in each vial. Add 2 drops of 6.0 M HCl to one vial, mix, note the color, and measure the pH. Add 2 drops of 6.0 M NaOH to the other vial, mix, note the color, and measure the pH. Record your data in the table.

HCl/NaOH Solutions		calculated pH	measured pH	observed color	pH after 6 M HCl color / pH	pH after 6 M NaOH color / pH
1	10 mL of 0.20 M HCl + 10 mL H ₂ O (buret)				X	X
2	10 mL of 0.20 M NaOH + 10 mL H ₂ O				X	X
3	10 mL 0.20 M HCl + 10 mL 0.20 M NaOH				/	/

Explain any differences between the calculated and measured pH values for solution #3 above.

Was solution #3 resistant to significant pH changes when small amounts of HCl or NaOH were added? Explain.

If a solution containing universal indicator was purple, would this solution be acidic, basic, or neutral?

5. Similar to the procedures used for the HCl/NaOH system (summary given below), **work with another group** and study the following systems. One group will study the acetic acid system while the other group will study the maleic acid system. Both groups will share data so record results and observations carefully. Make sure you and your group can answer the post-lab questions based on your data.

Read the reagent bottles carefully. Rinse all glassware between solutions.

Test the following solutions using this procedure:

- Prepare the solution below. Read the reagent bottles carefully.
- Add 3 drops of universal indicator to the solution. Mix. Record the color of the solution.
- Measure the pH of the solution.
- Place 10 mL each into 2 separate vials.
- Add 2 drops 6.0 M HCl to one vial, mix, note the color, and measure the pH.
- Add 2 drops 6.0 M NaOH to the other vial, mix, note the color, and measure the pH.
- Calculate the expected pH of the solution (do this later or during free moments in lab) and compare to the measured pH.

<i>Acetic Acid</i> Solutions	GROUP 1	calculated pH	measured pH	observed color	pH after 6 M HCl color / pH	pH after 6 M NaOH color / pH
4	Pipet 10 mL of 0.20 M CH ₃ COOH + 10 mL H ₂ O (buret)					
5	10 mL of 0.20 M CH ₃ COONa + 10 mL H ₂ O					
6	10 mL 0.20 M CH ₃ COOH + 10 mL 0.20 M CH ₃ COONa					
7	10 mL 0.0020 M CH ₃ COOH + 10 mL 0.0020 M CH ₃ COONa					

<i>Maleic Acid</i> Solutions	GROUP 2	calculated pH	measured pH	observed color	pH after 6 M HCl color / pH	pH after 6 M NaOH color / pH
8	Pipet 10 mL of 0.20 M NaC ₄ H ₃ O ₄ + 10 mL H ₂ O (buret)	4.10				
9	10 mL of 0.20 M Na ₂ C ₄ H ₂ O ₄ + 10 mL H ₂ O	9.65				
10	10 mL 0.20 M NaC ₄ H ₃ O ₄ + 10 mL 0.20 M Na ₂ C ₄ H ₂ O ₄					

Acetic Acid, CH ₃ COOH: $K_a = 1.75 \times 10^{-5}$ $pK_a = 4.76$	Maleic Acid, C ₄ H ₄ O ₄ : $K_{a1} = 1.26 \times 10^{-2}$ $pK_1 = 1.90$ $K_{a2} = 5.01 \times 10^{-7}$ $pK_2 = 6.30$
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Show your results to your instructor and redo any solutions with suspicious pH values.

6. Make sure you have collected a range of pH values (pH \approx 1–14) and their associated colors to answer Question #4 of the post-lab exercises. If necessary, prepare extra solutions of a given pH and add universal indicator.

Name(s) _____

Section _____

POST-LAB EXERCISES (from Lab Day 1)
Experiment 32

Submit your answers before starting the next part of the experiment.

1. Based on your observations in step 2 of the procedure, write down a chemical reaction that explains the pH change. What is produced as a result of blowing into a container of water? How would this affect the pH of the solution?
2. a. What are the characteristics of a chemical buffer: functional (how does it affect changes in physical properties) and chemical (what compound(s)/solution(s) are used to make a buffer)?

In lab, you prepared 10 different solutions. Based on the chemical definition, not your experimental results), which solutions were considered buffers (list the solution numbers)?

Buffer Solutions = _____

- b. Based on the functional definition, is solution #3 a buffer solution? Explain why or why not.
 - c. Based on your experimental results, which solution was the best at resisting pH change upon addition of small amounts of H^+ or OH^- (i.e., which had the largest buffer capacity)? How did you know this? Use your data to support your answer.
 - d. Using the Reservoir Analogy in the Introduction, explain how a buffer works to resist large pH changes.
3. Solutions #6 and #7 were prepared from CH_3COOH (acetic acid) and CH_3COONa (sodium acetate, the conjugate base of acetic acid). What part of the Reservoir Analogy (capacity, useful range or fill factor) explain why one of these solutions is a better buffer?

How does the Reservoir Analogy help to explain that buffers have limits as to how much they can resist pH changes? Use data to support your answer.

4. Universal indicator is an acid-base indicator which changes color with pH. Using your data as a guide, map out the color transitions, then answer the question below. You may need to estimate colors for some pH values.

Universal Indicator				
pH	observed color		pH	observed color
1			8	
2			9	
3			10	
4			11	
5			12	
6			13	
7			14	

Can an acid-base indicator, such as universal indicator, be used in place of a pH meter? Explain why or why not and any limitations.

5. Maleic acid, $C_4H_4O_4$, is a diprotic acid.
- How would you expand the Reservoir Analogy to describe a diprotic acid?
 - Give the two acid dissociation equilibria for maleic acid.

First Acid Dissociation Equilibrium Reaction:

Second Acid Dissociation Equilibrium Reaction:

Among the two reactions above, under the compound or ion, identify the strongest conjugate acid and strongest conjugate base.

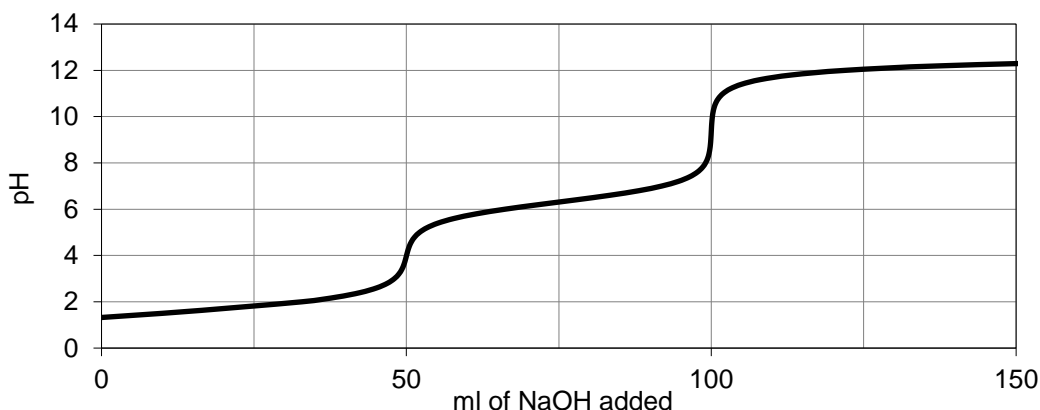
- What are the formulas for the sodium salts of the two conjugate bases.

First Acid Dissociation: _____

Second Acid Dissociation: _____

- Which acid dissociation equilibrium would solution #10 be associated with?
- How does your calculated pH and measured pH for solution #10 compare to each other?

Titration Curve of
50 mL 0.10 M Maleic Acid with 0.10 M NaOH



e. If universal indicator was added to the titration solution above, what color would the solution be at the *first equivalence point*? _____

What color would the solution be at the *second equivalence point* in the titration? _____

f. On the titration curve, circle the 2 buffer regions. On the graph, how does the slope within the buffer regions compare to slope at the equivalence points?

6. a. What would be the mole ratio of $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4/\text{NaC}_4\text{H}_3\text{O}_4$ in a $\text{pH} = 6.25$ buffer?

Maleic Acid: $\text{pK}_1 = 1.90$ $\text{pK}_2 = 6.30$ ($\text{pK}_a = -\log K_a$)

$$\text{pH} = \text{pK}_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

b. Assuming you wanted a total buffer concentration (i.e., $[\text{weak acid}] + [\text{conjugate base}]$) to be **0.100 M**, and a total volume of 50.0 mL, how many total moles would the solution have?

c. Using the ratio from 6a. and the moles from 6b., how many moles of each component of the pH = 6.25 buffer would you have?

d. Given the molar masses of the two sodium salts, ($\text{NaC}_4\text{H}_3\text{O}_4 = 138.05 \text{ g/mol}$; $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4 = 160.04 \text{ g/mol}$), and the value from 6c., what masses of each would you use to make 50.0 mL of a pH=6.25 buffer with a total buffer concentration of 0.100 M?

Mass of $\text{NaC}_4\text{H}_3\text{O}_4$ needed =

Mass of $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ needed =

e. If 0.0010 moles of NaOH are added to the buffer in part 6d., write the chemical reaction between the hydroxide ion and the appropriate component of the buffer. Would the pH increase, decrease or stay the same? How does the change in number of acidic protons in the proton reservoir (the buffer) compare to the change of conjugate base ions?

f. The number of moles of the components in part 6c. will change to what value upon the reaction in part 6e.? Use these calculated values to determine the new pH after the reaction in part 6e.

Experiment 32

BUFFERS

LAB DAY 2:

1. As a group, design and prepare a buffer according to the specifications provided by your instructor. Show your calculations below. Do not use a pH meter in your preparation of the buffer.

Buffer # _____

Specified target pH = _____

Calculations:

2. Let your instructor check over your calculations and obtain the necessary acid salts.

Instructor's initials _____

3. Prepare your buffer. Report your experimental procedure below (give the exact amounts and glassware used). Do not use a pH meter in your preparation.

Procedure for preparing your buffer:

4. Have your instructor test the pH of your prepared buffer solution. Because we have ignored ionic effects in our calculations (a more advanced topic), the pH measured with a meter will be *lower* than the target pH. Add 0.40 pH units to the measured pH. Is this value close to the specified target pH?

Save this solution for the next part of the lab.

Measured pH =

Measured pH + 0.40 =

Name _____

Section _____

Date _____

PRE-LAB QUESTIONS
Experiment 32

Read the experiment and complete this assignment **before** Day 1 of the lab.

1. Predict the pH of the following solutions that you will prepare in this experiment. Assume 25°C.

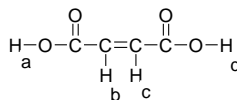
- | | | | |
|--|-----------|-----------|-----------|
| a. 0.10 M HCl | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| b. 0.10 M NaOH | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| c. 0.10 M CH ₃ COOH | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| d. 0.10 M CH ₃ COONa | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| e. 0.10 M Na ₂ C ₄ H ₂ O ₄ | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| f. 10 mL 0.20 M HCl mixed with 10 mL 0.20 M NaOH | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| g. 10 mL 0.20 M CH ₃ COOH mixed with 10 mL 0.20 M CH ₃ COONa | a. pH < 7 | b. pH = 7 | c. pH > 7 |
| h. distilled water that has been exposed to the atmosphere. | a. pH < 7 | b. pH = 7 | c. pH > 7 |

2. a. Calculate the pH of a 0.20 M HCl solution

2. b. Calculate the pH of the solution prepared by mixing 10.0 mL of 0.20 M HCl and 10.0 mL of distilled water.

3. a. Calculate the pH of a 0.10 M CH₃COOH solution. K_a of CH₃COOH = 1.76×10^{-5} .

3. b. Calculate the pH of a 0.10 M CH₃COO⁻ Na⁺ solution. (Think about whether this is an acidic or basic solution.)



4. The structure for maleic acid (C₄H₄O₄) is:

Which are the acidic hydrogens that are removed during deprotonization of this acid? (See labels on figure.)
Select **ALL** that apply.

- a. H_a b. H_b c. H_c d. H_d