Experiment 3: Acids, Bases, and Buffers

Reading: *Chemistry the Central Science*, Chapter 16.1-16.7

Introduction:

The reaction of an acid and a base is a *neutralization* reaction. The technique of accurately measuring the volume of solution, such as a strong base, required to react with another reagent, such as a weak acid, is termed a *titration*. The neutralization titration in this experiment is the reaction of an unknown weak acid, HA, with NaOH:

$$HA\ (aq) + OH^-\ (aq) \rightarrow A^-\ (aq) + H_2O \qquad (1)$$

An acid-base titration can be monitored either through the use of an acid-base indicator or through the use of a pH meter. Monitoring the pH during titration of a weak acid with a strong base leads to a titration curve, Figure 1. The equivalence point occurs when enough base has been added to react completely with all of the weak acid originally in solution. As can be seen in equation (1), the predominant species in solution at the equivalence point is the conjugate base A^-. This conjugate base reacts with water to give a basic solution at the equivalence point:

$$A^-\ (aq) + H_2O \rightleftharpoons HA\ (aq) + OH^-\ (aq) \qquad (2)$$

For a weak acid, the pH is not neutral at the equivalence point but is greater than 7.0. The equivalence point can be found as the steepest portion of the titration curve as seen in Figure 1. At the equivalence point, the moles of strong base added is equal to the moles of weak acid being titrated:

$$M_tV_t = M_xV_x \qquad (3)$$

where M_t is the concentration of the titrant, V_t is the volume of added titrant, M_x is the concentration of the unknown weak acid, and V_x is the volume of the weak acid that is titrated.

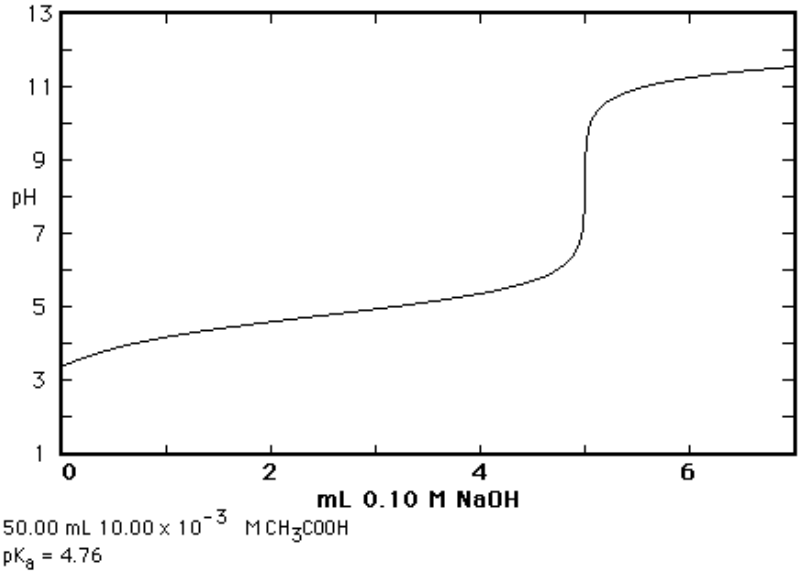


Figure 1. Titration of a weak acid with strong base, NaOH.

The equivalence point (or the end point) of the titration can be estimated visually, as in Figure 1. A more accurate approach is to calculate the derivative (d pH/dV) of the titration curve and plot this function versus volume of added base. As shown in Figure 2, the derivative plot exhibits a clear maximum at the equivalence point.

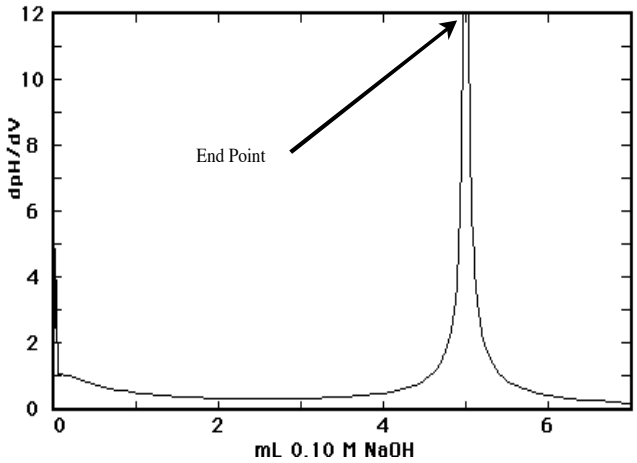


Figure 2. Derivative plot of the acetic acid titration shown in Figure 1.

The derivative of the titration curve is approximated by the finite differences:

$$\frac{d\,pH}{dV} \cong \frac{\Delta pH}{\Delta V} = \frac{pH_2 - pH_1}{V_2 - V_1} \qquad (4)$$

where pH_1 is the measured pH at added volume V_1 and pH_2 is the measured pH at added volume V_2. The derivative is calculated with successive pairs of data points, Table 1.

Table 1: Calculation of the derivative of an example titration curve.

V (mL) NaOH	pH	ΔpH/ΔV	
10.32	3.86	0.5	
10.44	3.92	0.83	
10.56	4.02	1.25	
10.68	4.17	2.58	*(equivalence point)*
10.80	4.48	1.58	
10.92	4.67		

Another significant volume during a titration is when the number of moles of acid (HA) remaining is exactly equal to the number of moles of conjugate base (A^-) produced. This point is called the "half-equivalence point" because it occurs when exactly half the weak acid has been titrated. From the Henderson-Hasselbalch equation (5), the half-equivalence point gives pH = pK_a.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad (5)$$

Primary Standards

Preparation of Standardized 0.10 M NaOH

A solution of NaOH with accurately determined concentration is used as the titrant in this experiment. Solutions of NaOH readily absorb CO_2 from the atmosphere:

$$CO_2\,(g) + 2\,OH^-\,(aq) \rightarrow CO_3^{2-} + H_2O\,(l) \qquad (6)$$

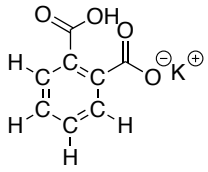
This reaction changes the concentration of the hydroxide, so precautions are necessary to minimize the effect. The formation of CO_3^{2-} ions in the solution also interferes with the equivalence point, by decreasing the slope of the titration curve at the equivalence point. Solutions must be kept covered while in use and tightly stoppered in storage. The absorption of CO_2 must also be avoided when preparing the solution. Solutions of sodium hydroxide slowly attack glass containers and cause glass stoppers to become stuck. Thus, sodium hydroxide solutions are usually stored in polyethylene bottles. Also, burettes or titration pumps must be thoroughly cleaned immediately after use.

Primary Standards

Laboratory work frequently involves the use of a standardized solution, which is a solution of accurately known concentration. You will use a standardized solution of NaOH for the titration of a weak acid. The concentration is roughly 0.10 M, but the concentration will be determined to better than three-significant figures. The concentration of the NaOH solution is determined by titration against a primary standard. For a substance to be a primary standard, the following criteria should be met. A primary standard substance should be:

- Available in very pure form
- Reasonably soluble
- Stable in the pure form and in solution
- Nonhygroscopic (doesn't absorb water from the air) and easily dried
- A compound with a reasonably high formula weight

Few substances meet these criteria, so the number of useful primary standards is quite limited. Two common primary standard bases are pure sodium carbonate and borax. The primary standard acid in this experiment is KHP, which is the monoprotic potassium salt of a diprotic carboxylic acid, $KHC_8H_4O_4$:



The accurate concentration of your sodium hydroxide solution is determined by titration of accurately known masses of KHP. The reaction for the standardization titration is:

$$KHC_8H_4O_4\,(aq) + NaOH\,(aq) \rightarrow KNaC_8H_4O_4\,(aq) + H_2O(l) \qquad (7)$$

To determine the exact concentration of the sodium hydroxide solution, the number of moles of sodium hydroxide that react completely with the known number of moles of KHP is calculated. The number of moles of KHP is equal to the number of moles of added base at the equivalence point: M_tV_t = moles KHP, where M_t is the concentration of the titrant and V_t is the volume of

added titrant. You then use this standardized NaOH solution for the titration of the weak acid in Part E of this lab.

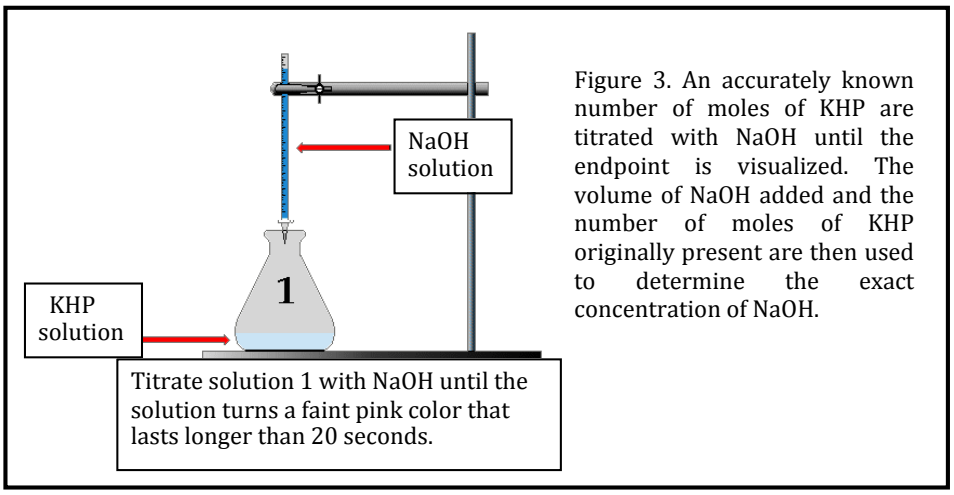


Figure 3. An accurately known number of moles of KHP are titrated with NaOH until the endpoint is visualized. The volume of NaOH added and the number of moles of KHP originally present are then used to determine the exact concentration of NaOH.

Summary of Experiment

Your goals for the three weeks in order are as follows:

- Standardize a solution of NaOH with the primary standard KHP to determine the exact concentration of NaOH.
- Use the standardized NaOH solution to titrate the unknown weak acid to determine its identity and concentration. The list of possible weak acids will be provided in the laboratory.
- Make an optimum buffer a variety of ways.

Procedure:

Week 1- Standardization of NaOH of Unknown Concentration (March 6-10)

Part 1. Doing titrations

1. Carefully transfer about 0.7 to 0.9 grams of dry KHP (potassium hydrogen phthalate) into a tared weigh vial. Record the exact mass of KHP.

2. Dissolve each sample in about 30-50 mL of deionized water, after rinsing into a 200 or 250 mL Erlenmeyer flask. Add eight drops of phenolphthalein indicator solution.

3. Obtain 1 L of unknown NaOH. Mix thoroughly (on stir plate) to make sure you have a homogeneous solution.

4. Rinse your burette with your assigned NaOH solution. Make sure that the rinse solution comes in contact with the entire inner surface of the burette and the tip of the burette. Drain rinse into a small beaker.

5. Close the burette stopcock and fill the burette with NaOH to above the top calibration mark on the burette. Lower the meniscus of the solution until it reaches a calibrated portion of the

burette. Make certain that the burette tip is completely filled with the solution. Record the initial burette reading to the nearest 0.01 mL, using a piece of white paper behind the burette to visualize the meniscus, if necessary.

6. Place this Erlenmeyer flask under the burette, on top of a stir plate. Lower the burette tip until it is into the flask, as shown in Figure 3.

7. Turn on the stirrer so that it is gently mixing and add the NaOH slowly to the solution while mixing.

8. As the titration progresses, the approach of the endpoint will be signaled by brief flashes of pink. At this point, add the NaOH drop wise to the KHP solution. As the endpoint is approached more closely, these temporary flashes of color will persist longer and fractional parts of a drop of NaOH should be added. Fractions of a drop may be added by allowing a droplet of NaOH to begin to form on the burette tip. After touching the burette tip to the inner surface of the flask, wash down the inner surface of the flask with a stream of deionized water from a wash bottle. The titration is complete when the indicator exhibits a pink color that persists for several seconds. Wait for about 15-20 seconds to allow any solution on the inner wall of the burette to drain down to the meniscus and then read the final burette volume to the nearest 0.01 mL.

9. Repeat the titration process two more times, as you'll need three successful trials.

10. Perform the following calculations to determine whether you need to do another titration.

    - In Excel, calculate the concentration (mol/L) of NaOH for each of your 3 trials.

    - Calculate the average concentration of NaOH, the standard deviation of your data, and the relative standard deviation. If after all of these measures, you are still not within 1%, you will continue to titrate until you meet this requirement or run out of time.

11. After the titration work is completed, drain and *thoroughly rinse* the burette with deionized water and leave it hanging upside down on the burette stand. Thoroughly wash all other glassware used in this experiment. Write your calculated average molarity on your NaOH bottle. Please place bottle on front lab table for storage, before you leave. Please do not put this bottle in a lab drawer.

Part 2: Calibrate a pH Meter

The second goal for today is to learn how to calibrate and operate a typical laboratory pH meter. The procedure for operating every pH meter is slightly different. The ones we have in lab are fairly self-explanatory so we would like you to independently figure out how to calibrate the lab pH meters. However, before you begin, it is universally true that for a pH electrode to work correctly, the filling hole near the top of the electrode must be open. Since the filling hole should be kept closed when the meter is not in use in order to prevent evaporation of the solution inside the electrode, the first thing you should always do when operating a pH meter is to open the filling hole. The last thing you should do is to close the filling hole. Note that if you can't SEE a hole, then the hole is not open. Turning the blue-collar sleeve at the top of the probe can open it.

After you have opened the filling hole, use all three provided standard pH buffers of 4.0, 7.0, and 10.0 to calibrate the meter. Make sure that the electrode is completely immersed in solution when you are measuring pH (the electrode is the small glass "eye" or bump near the tip of the pH probe). You can adjust the level of the probe by using the lever arm to position it- you should never directly handle the probe itself (unless you are opening or closing the filling hole). Record the calibration procedure in your lab notebook in sufficient detail that you or someone else could follow your instructions to calibrate this meter.

Following successful calibration of the meter, noted by the %slope value you want to record in your lab notebook, measure a provided mystery solution of unknown pH. Measure the pH of the unknown and confirm this value with your lab instructor. Record which mystery solution you tested. Upon confirmation of your measurement, you will be assured that you are correctly using the pH meter. Whenever the probe is not being used to make a measurement please keep it submersed in container labeled "probe storage solution". Are you finished? Please pour the wastewater container into the sink. Place the pH probe in the provided water beaker.

Make sure you have all the relevant data documented before you leave lab – check with your lab instructor!

Week 2- Titration of Unknown Weak Acid (March 13-17)

Part I. This week you will perform a titration of an unknown weak acid with the NaOH solution that you standardized last week. You will determine the pK_a of this acid through the half-equivalence point of the titration and the concentration of the acid through the equivalence point. You will use an automated titration system to perform a replicate pair of titrations for your unknown weak acid. In this system, a precision pump replaces the burette used in traditional titrations. A computer controls the pump to deliver titrant to the reaction vessel. A pH meter is used to measure the pH, and these data are recorded by the computer for display and analysis.

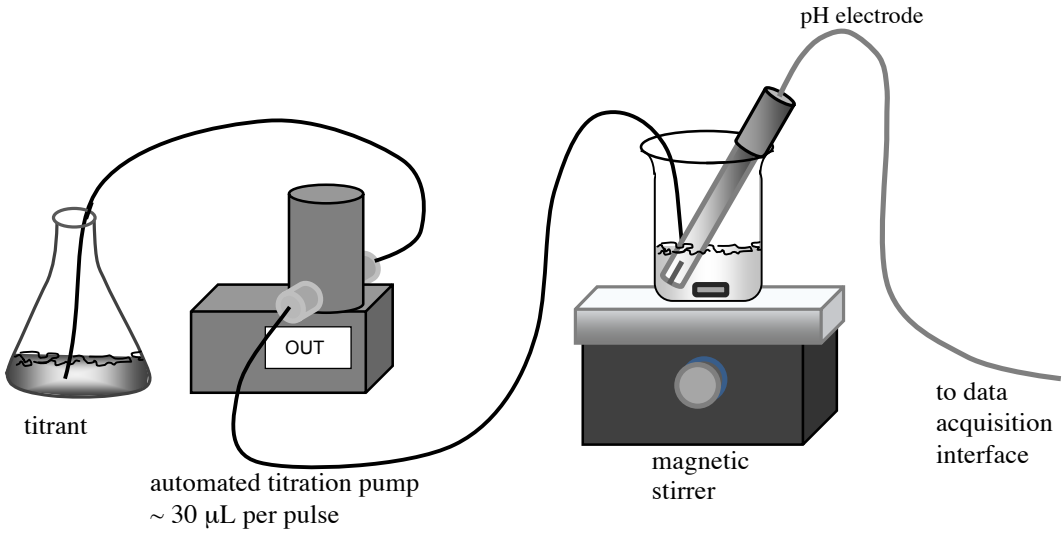


Figure 4. The automated titration system is based on a computer controlled titration pump. The progress of the titration is monitored using a pH electrode.

1. Follow the directions on the Vernier LabPro Instructions (provided at each instrument) to calibrate your pump and pH probe.
2. Perform the titration as described in the Vernier LabPro Instructions using your assigned unknown acid to be identified. Be sure to record any markings on the container of your unknown acid.
3. Repeat the titration with the same unknown weak acid to find the average molarity of the two trials.
4. Analyze your data as described in the Vernier LabPro Instructions.
5. Turn in a written copy of your acid identity and average acid molarity to your lab instructor. See specific instructions at top of page 6 of this handout.
6. Return your NaOH bottle to the front table for storage before you leave.

To outline the procedure for this work you will need to carefully read the Vernier Handout provided in lab. The Vernier handout is a combination of computer instructions and experiment related procedure. Remember computer instructions and data analysis are not needed for a procedure. You just need to provide a sufficient outline of the experimental procedure in your lab notebook.

Part II: Investigation of Buffers: Testing Factors that Affect Buffers

One of the goals of your work will be to produce buffers from your weak acid and the NaOH solution but to also create buffers from any given reagent or salt. Prior to doing this you first need to investigate what factors will or won't affect buffers.

A. Comparing the pH of Different Ratios (Recipes) of Weak Acid to Conjugate Base

1. Prepare about 50 or 30 mL of 3 different solutions with the following ratios of 0.50 M sodium acetate to 0.50 M acetic acid: 10/1; 1/1; 1/10. **Keep the 1:1 solution until you are completely finished with this experiment- you will use it multiple times.**

2. Measure the pH of each of these solutions. *10:1 pH_____ 1:1 pH_____ 1:10 pH_____*

B. Comparing Dilution of Buffer to Dilution of Buffer Components

1. Take 2 mL of the 1/1 solution. Dilute this solution by a factor of 10 by mixing it with 18 mL of deionized water. Measure its pH.

   1:1 pH____ (from part A) 1:1 solution diluted 10x's pH_____

2. Measure the pH of a sample of the stock 0.50 M acetic acid. Dilute it by a factor of 10, and measure the pH of this dilution.

   0.50M $HC_2H_3O_2$ pH_____ 0.50M $HC_2H_3O_2$ diluted 10x's_____

3. Repeat step 2 with the stock 0.50 M sodium acetate solution.

   0.50M $NaC_2H_3O_2$ pH_____ 0.50M $NaC_2H_3O_2$ diluted 10x's_____

C. Comparing how much pH changes upon Addition of Strong Acid or Base

1. Measure the pH of the laboratory deionized water. Note that an approximate pH is fine. It is not necessary to wait several minutes for the pH reading to stabilize. *H_2O pH _____*

2. To 20 mL of this water, add 10 mL of 0.10 M HCl. Measure the pH. Again, an approximate pH reading is fine. *H_2O & HCl pH _____*

3. To 20 mL of water, add 10 mL of your ~0.10 M NaOH. Measure the pH.
   H_2O & NaOH pH _____
4. To 20 mL of the 1/1 solution of sodium acetate/acetic acid (the original solution- not the dilution), add 10 mL of the 0.10 M HCl. Measure the pH.
   1:1 pH____ (from part A) 1:1 & HCl pH _____

5. To 20 mL of 1/1 solution of sodium acetate/acetic acid, add 10 mL of ~0.1 M NaOH. Measure the pH. *1:1 pH____ (from part A) 1:1 & NaOH pH _____*

Make sure you have all the relevant data documented before you leave lab – check with your lab instructor!

Week 3- Investigation of Buffers (March 27- March 31)

Part I: Creation of Buffers

A. Making a Weak Acid and Conjugate Base Buffer , Buffer #1

Looking at your notes from Week 2 you have already documented the effectiveness of the acetic acid: sodium acetate 1:1 buffer. In a 1:1 molar ratio the pH = pKa. At this point, you have determined both the identity of your weak acid and its pK_a. The pK_a dictates the pH at which a weak acid can act as a good buffer. Use your weak acid and it's respective conjugate base to create an effective buffer. Then test it using the three factors from week 2 of Exp #3. Here are some guidelines:

1. Based on your calculated concentrations of your weak acid, determine the volume of conjugate base needed to add to 20 mL of your weak acid to achieve a 1:1 ratio of weak acid: conjugate base. Record calculations in lab notebook. Make up one beaker containing such a solution that will be called Buffer #1.

2. Measure the pH of this solution. B*uffer #1 pH* ____ Does it equal the pKa? *yes/no* _____
   If no, remake buffer until pH = pKa.
   Record modified buffer recipe. *Volume ratio weak acid : strong base* _____

3. To test resistance of buffer for dilution take 2 mL of the Buffer #1 solution and put into a clean 30 mL beaker. Dilute this solution by a factor of 10 by mixing it with 18 mL of deionized water. Measure its pH.
   Buffer #1 pH____ (from step 2) Buffer #1 diluted 10x's pH_____

4. To test effectiveness of Buffer #1 for added strong acid add 1mL of 0.1 M HCl to the beaker of buffer from step 2 and record the pH.

Buffer #1 pH _____ (from step 2) *Buffer #1 & HCl pH* _____

5. To test effectiveness of Buffer #1for added strong base add 2mL of 0.1 M NaOH to the beaker of buffer from step 4 and record the pH.
   Buffer #1 pH _____ (from step 2) *Buffer #1 & NaOH pH* _____

B. Making a Weak Acid Buffer without available Conjugate Base, Buffer #2

At this point, you have determined both the identity of your weak acid and its pK_a. The pK_a dictates the pH at which a weak acid can act as a good buffer because an equal amount of its conjugate base will also be present. Unfortunately, a conjugate base solution may not always be readily available. You are assigned the task of creating the conjugate base from NaOH, which is provided from week 1. Use your weak acid and NaOH to create an effective buffer and then test it using the three factors from week 2 of Exp #3. Here are some guidelines:

1. Based on your calculated concentrations of your weak acid, determine the volume of NaOH (~0.10 M) that you would need to add to 20 mL of your weak acid to achieve a 1:1 ratio of weak acid: conjugate base. Look back at your notes for Week 2 of Exp 3. Record calculations in lab notebook. Make up one beaker containing such a solution that will be called Buffer #2.

2. Measure the pH of this solution. B*uffer #2 pH* ____ Does it equal the pKa? *yes/no* _____
   If no, remake buffer until pH = pKa.
   Record modified buffer recipe. *Volume ratio weak acid : strong base* _____

3. To test resistance of Buffer #2 for dilution take 2 mL of Buffer #2 solution and put into a 30 mL beaker. Dilute this solution by a factor of 10 by mixing it with 18 mL of deionized water. Measure its pH.
   *Buffer #2 pH____ (from step 2) Buffer #2 solution diluted 10x's pH*_____

4. To test effectiveness of buffer for added strong acid add 1mL of 0.1 M HCl to the beaker of buffer from step 2 and record the pH.
   Buffer#2 pH _____ (from step 2.) *Buffer #2 & HCl pH* _____

5. To test effectiveness of buffer for added strong base add 2mL of 0.1 M NaOH to the beaker of buffer from step 4 and record the pH.
   Buffer #2 pH _____ (from step 2.) *Buffer #2 & NaOH pH* _____

C. Making Buffers on a Budget , Buffer #3 & #4

How do you make an optimum buffer when a lack of money or availability might force you to be creative? This next challenge requires you to create your own weak acid/weak base from an available salt. The salt must first be chosen to match its pKa to the desired buffer pH, as close as possible. Secondly, the salt must be made into a usable solution. Thirdly, with no conjugate base/conjugate acid available you will need to create the conjugate from 0.10M HCl or 0.10M NaOH; whichever is appropriate. There are two salts in the inventory room- sodium acetate trihydrate and ammonium chloride. Your goal is to make one buffer at a pH of exactly 9.0 and

one buffer at a pH of exactly 5.0. Your success will be dependent on the test for the resistance to dilution and effectiveness of each to resist strong acid, then strong base.

1. First, identify which of the two available salts will make a weak acid solution and which will make a weak base solution. Secondly, pair the solution to the correct reagent for making a buffer.
   The identity of the weak acid is:_____
   The conjugate base of this weak acid will be created using which solution? _____
   At which assigned pH will this buffer work best? _____
   The identity of the weak base is: _____
   The conjugate acid of this weak base will be created by using which solution? _____
   At which assigned pH will this buffer work best? _____

2. You want to make 100.0 mL of 0.10M sodium acetate trihydrate and 100.0 mL of 0.10M ammonium chloride. Calculate how much of each weak acid/weak base salt to measure (in grams) to make an effective buffer with each. Show calculations in your notebook. Show your lab instructor the grams you will be measuring out for each before going to the balance room.

3. Determine the volume of reagent needed to add to 20 mL of 0.1M sodium acetate trihydrate in a beaker to achieve the assigned pH. Record calculations in lab notebook.

4. Make up one beaker containing such a solution that will be called Buffer #3.

5. Measure the pH of this solution. *Buffer #3 pH* ____
   Does it equal the assigned pH from step 1? *yes/no* _____
   If no, remake buffer until pH = assigned pH. Record modified buffer recipe.
   Volume ratio (in mL) _____

6. To test resistance of Buffer #3 for dilution take 2 mL of Buffer #3 solution and put into a 30 mL beaker. Dilute this solution by a factor of 10 by mixing it with 18 mL of deionized water. Measure its pH.
   Buffer #3 pH____ (from step 5) *Buffer #3 solution diluted 10x's pH_____*

7. To test effectiveness of Buffer #3 for added strong acid add 1mL of 0.1 M HCl to the beaker of buffer from step 5 and record the pH.
   Buffer #3 pH _____ (from step 5) *Buffer #3 & HCl pH* _____

8. To test effectiveness of Buffer #3 for added strong base add 2mL of 0.1 M NaOH to the beaker of buffer from step 6 and record the pH.
   Buffer #3 pH _____ (from step 5) *Buffer #3 & NaOH pH* _____

9. Determine the volume of reagent needed to add to 20 mL of 0.1M ammonium chloride in a beaker to achieve the assigned pH. Record calculations in lab notebook.

10. Make up one beaker containing such a solution that will be called Buffer #4.

11. Measure the pH of this solution. *Buffer #4 pH* ____
    Does it equal the assigned pH from step 1? *yes/no* _____
    If no, remake buffer until pH = assigned pH. Record modified buffer recipe.
    Volume ratio (in mL) _____

12. To test resistance of Buffer #4 for dilution take 2 mL of Buffer #4 solution and put into a 30 mL beaker. Dilute this solution by a factor of 10 by mixing it with 18 mL of deionized water. Measure its pH.
    Buffer #4 pH____ (from step 11) *Buffer #4 solution diluted 10x's pH_____*

13. To test effectiveness of buffer for added strong acid add 1mL of 0.1 M HCl to the beaker of buffer from step 11 and record the pH.
    Buffer #4 pH _____ (from step 11) *Buffer #4 & HCl pH* _____

14. To test effectiveness of buffer for added strong base add 2mL of 0.1 M NaOH to the beaker of buffer from step 13 and record the pH.
    Buffer #4 pH _____ (from step 11) *Buffer #4 & NaOH pH* _____

Make sure you have all the relevant data documented before you leave lab – check with your lab instructor!

Laboratory Report: Use the provided Report Form for this experiment.