Experiment 8 and 9
Weak Acids and Bases: Exploring the Nature of Buffers

Pre-Laboratory Assignments
Reading:
  Textbook
    • Chapter 16
    • Chapter 17:1-3
  This Laboratory Handout

Pre-Laboratory Assignments: Complete the following questions using Excel and bring the answers with you to lab. There are two questions for Week 1 and one question for Week 2. Your spreadsheet must be easy to follow and you must use Excel (rather than a calculator) to do the calculations.

Week 1
Question 1: Calculate the molarity of a NaOH solution of which 32.6 mL is required to neutralize 0.854 g KHP (Potassium Hydrogen Phthalate; FW = 204.227 g/mol).

Question 2: a) Using Excel, plot the following data for the titration of a 10.0 mL solution of a weak acid by 0.100 M NaOH. b) Use the graph to predict the pK_b of the weak acid and the analyte concentration (explain your methodology in text in your Excel file).

<table>
<thead>
<tr>
<th>mL NaOH</th>
<th>pH</th>
<th>mL NaOH</th>
<th>pH</th>
</tr>
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<td>10.95</td>
</tr>
</tbody>
</table>

Week 2
You wish to make up a 0.100 M solution of ‘Tris’ buffer at pH 8.0. Tris is a weak base with a pK_b of 5.9 and a formula weight of 121.1 g/mol.

a) What mass of Tris do you need to make up 100.0 mL of a 0.100 M solution?
b) What reagent must you add to the solution of Tris base to create a buffer?
c) If the reagent from part ‘b’ was available as a 1.0 M solution, what volume would you need to add to your Tris solution to make the specified buffer?
Introduction

Acid-Base Chemistry
The strength of a Bronsted-Lowry acid is related to its ability to act as a proton donor in water. The general form of the ionization reaction that occurs when an acid is dissolved in water is:

\[
\text{HA (aq) + H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{A}^- (aq) \quad (1)
\]

A strong acid is one for which this equilibrium lies, essentially, all the way to the right. For example, the strong acid HCl is completely dissociated in aqueous solution so that for 0.1 M HCl, the \([\text{H}_3\text{O}^+]=0.1\) M. By contrast, a weak acid is one for which this equilibrium lies far to the left, indicating only partial dissociation. Both undissociated HA and its conjugate base A\(^{-}\) are present in solution. The equilibrium constant associated with this reaction is therefore small:

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \ll 1
\]

Solutions containing a weak acid and its conjugate base have important applications in a number of areas. For example, biological systems must operate within a very narrow range of pH. This is possible through the use of an appropriate weak acid and its conjugate base, which provide the ability to buffer against changes in pH. During this experiment you will investigate the reaction of a weak acid HA with a strong base, which results in the formation of water and the conjugate base A\(^{-}\) and can lead to a buffer under appropriate conditions.

\[
\text{HA (aq) + OH}^- (aq) \rightarrow \text{A}^- (aq) + \text{H}_2\text{O} \quad (2)
\]

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 titration. 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 curve such as that shown in Figure 1.

A significant point in the titration of a weak acid with a strong base is the “equivalence point,” when enough base has been added to react completely with all of the weak acid originally in solution. As can be seen in equation (2), the predominant species in solution at the equivalence point is the conjugate base A\(^{-}\). This base reacts with water as follows:

\[
\text{A}^- (aq) + \text{H}_2\text{O} \rightleftharpoons \text{HA (aq) + OH}^- (aq) \quad (3)
\]

Thus, 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. Therefore, titrations can be used to determine the concentration of either the acid or base as long as the concentration of the other reagent is accurately known.
The end point of the titration can be estimated visually, as in Figure 1. A more accurate approach is to calculate the derivative (dpH/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 end point. The end point of a titration is what we can “see” analytically. If you are careful in your experimental design, the end point will be very close to the equivalence point.

Another significant point 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 (4) it can be seen that at the half-equivalence point, pH = pKₐ. Thus, one could use this equation to calculate the pKₐ of a weak acid given the pH of the solution when exactly half the weak acid has been titrated at the half-equivalence point.

$$pH = pK_a + \log \frac{[A]}{[HA]}$$  \hspace{1cm} (4)
Primary Standards

In order to be as accurate as possible during a titration, chemists usually first determine the concentration of the titrant (the sodium hydroxide, in your case) by calibrating it with a **standard solution**, a solution of accurately known concentration. You will use a primary standard during the first week to standardize the sodium hydroxide solution that you will use in the titration of the unknown weak acid. 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 pick up water from the air) and easily dried
- A compound with a reasonably high formula weight

Not very many 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. Some primary standard acids are potassium hydrogen phthalate (KHP), oxalic acid dihydrate, sulfamic acid, and benzoic acid. The primary standard acid we will use in this experiment is KHP (1), the monoprotic potassium salt of a diprotic carboxylic acid (KHC₈H₄O₄).

![Diagram of KHC₈H₄O₄](image)

During the first week, you will accurately determine the concentration of a sodium hydroxide solution by titration of KHP solutions containing accurately known masses of KHP. The sodium hydroxide solution is referred to as the **tirant** because it is the solution dispensed from the burette into the solution being titrated. The reaction involved in this titration is shown in Equation (5).

\[
\text{KHC}_8\text{H}_4\text{O}_4 \text{(aq)} + \text{NaOH (aq)} \rightarrow \text{KNaC}_6\text{H}_4\text{O}_4 \text{(aq)} + \text{H}_2\text{O(l)}
\]  

(5)

To determine the exact concentration of the sodium hydroxide solution, the number of moles of sodium hydroxide that react completely with a known number of moles of KHP must be calculated. A small amount of indicator solution containing phenolphthalein is added to each standard acid solution and signals the endpoint of the titration by changing color. Phenolphthalein is colorless in the acid solution but changes to pink at the endpoint of the titration. The number of moles of KHP (which equals the number of moles of base) divided by the volume of base added to reach the endpoint gives the exact concentration of the base. You will need to know this concentration for the titration of the weak acid that you will perform during the second week. A cartoon of the procedure that you will follow is given in Figure 3.
Solutions of sodium hydroxide used for these titrations slowly attack glass containers and cause glass stoppers to become stuck. Thus, sodium hydroxide solutions are usually stored in polyethylene bottles. Also, burettes must be thoroughly cleaned immediately after use.

Figure 3. An accurately-known number of moles of KHP is 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

During the course of this two-week experiment, you will use the properties of weak acids to identify an unknown weak acid and its concentration. You will then use your weak acid to produce a buffer and also create a second buffer from reagents present in the lab. Your goals are as follows:

- Standardize the solution of NaOH with the primary standard KHP (1) to determine the exact concentration of NaOH. (Week 1) Use your pre-lab exercise to help you with this!
- Use the standardized NaOH solution to titrate the unknown weak acid to determine its identity and concentration. (Week 1) Use your pre-lab exercise to help you with this!
- Investigate the properties of buffers and then use your weak acid and NaOH to produce a buffer. (Week 2)

Experimental Procedure

You will work in pairs for this experiment. During Week 1, each group should perform at least three titrations of their own sample of unknown NaOH.

For this laboratory exercise, you should obtain a precision ≥ 99%. If the precision is too low, more titration trials may need to be performed to achieve a 1% relative standard deviation. **Notes:** If you have an obvious experimental error and need to repeat a trial, you may reject the trial. However, if you simply have low precision and are doing multiple titrations, you must include all the titrations in the data analysis. If you think there is an outlier, a quality statistical test (Q-test) can be performed to identify if it is valid data point or if it can be rejected.
Week 1 Part A - Standardization of NaOH of Unknown Concentration

1. Carefully transfer about 0.7 to 0.9 grams of dry KHP (potassium hydrogen phthalate) into a tared, clean 200- or 250- mL Erlenmeyer flask. Record the weight to the nearest 0.1 milligram. Each individual should prepare three such samples.

2. Dissolve each sample in about 30-50 mL of deionized water. Add eight drops of phenolphthalein indicator solution to the contents of each flask.

3. Obtain 1 liter of unknown NaOH. Mix thoroughly to make sure you have a homogeneous solution.

4. Clean your burette, and then rinse it with three 5-mL portions of NaOH. Make sure that the rinse solution comes in contact with the entire inner surface of the burette and the tip of the burette.

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 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.

6. Place one of the Erlenmeyer flasks containing the KHP solution under the burette on top of a stir plate, add a magnetic stirrer, and lower the burette tip until it is well into the mouth of the flask, as shown in Figure 3.

7. Turn on the stirrer (NOT the heating element) so that it is gently mixing and add the NaOH slowly to the solution with 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 distilled 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 with the other 2 samples of KHP.

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 should perform a couple more trials to obtain 1% error, or 99% precision. You must check with your instructor to ensure you have successfully completed the titrations. Once your instructor checks your work, you may continue.

11. When all of the titrations are 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. **Label your standardized NaOH with your name, lab section, and standardized Molarity.** Save your NaOH solution for week two.

**Using a pH Meter** (work together as a pair)

Another goal for today is to learn how to 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. It can be opened by turning the dial at the top of the probe in the “open” direction.

After you have opened the filling hole, use standard pH buffers of 4.0 (usually pink), 7.0 (usually yellow), and 10.0 (usually green or blue) 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, obtain a solution of unknown pH from your instructor. Measure the pH of the unknown and confirm this value with your instructor. Upon confirmation of your measurement, you will be assured that you are correctly using a pH meter. Rinse the electrode with distilled water, and cap the pH electrode.

**Data that should be included in your notebook:**
- Amount of KHP, initial volumes, final volumes of NaOH titration.
- Standardized NaOH molarity, recorded values for data analysis.
- Excel tables, graphs, figures, or charts.
- Thorough observations and analyses of all your experiments.

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**Week 2 – Investigation of Buffers**

One of the original goals is to produce a good buffer from your weak acid and the NaOH solution. Prior to doing this, you will use the model system of acetic acid and its conjugate base acetate (as sodium acetate) to investigate some of the factors that affect a buffer solution.

**Week 1 Part B- Titration of Unknown Weak Acids with Standardized NaOH**

This week you will also perform a titration of an unknown weak acid with the NaOH solution that you just standardized in week one. 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.

Setup the titration system shown in Figure 3 with the addition of a pH electrode. Instead of KHP as the analyte, you will titrate two unknown weak acids (each partner gets their own
weak acid). Titrate both weak acids recording pH as a function of added NaOH. **It is important that you record volume of NaOH and pH after each addition of base.**

**Part 2: Factors that Affect Buffers** (work together as a pair)

**A. pH of Different Ratios of Weak Acid/Conjugate Base**
1. Prepare about 50 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. Standardize a pH meter and measure the pH of each of these solutions in a 50-mL beaker. (You do not have to use all 50 mL of your solution; make sure you don’t overflow the beaker.)

**B. Effect of Dilution**
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 (in a 30-mL beaker).

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.

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

**C. Effect of 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.*

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.

3. To 20 mL of water, add 10 mL of your ~0.10 M NaOH. Measure the 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.

5. To 20 mL of **FRESH** 1/1 sodium acetate/acetic acid, add 10 mL of ~0.1 M NaOH. Measure the pH.

**D. Analysis of Results**
- For your Part A data, use the Henderson-Hasselbalch equation to calculate the expected pH of each solution you tested. How well do your measured values agree with the expected values?
- From your Part B data, what is unique about a mixture of a weak acid/conjugate base relative to the weak acid or conjugate base alone?
- From your Part C data, how does a mixture of a weak acid/conjugate base respond to added acid or base relative to water?
Part 3: Creation of Buffers (work individually for Part 3)

A. Using your Weak Acid
At this point, you have determined both the identity and pKₐ of two weak acids. The pKₐ 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. Use your weak acids to create buffers as follows (one partner uses one of the weak acids, another does the other):

1. Based on your calculated concentrations of the weak acid, determine the volume of your NaOH (~0.10 M) that you would need to add to 50 mL of your weak acid to achieve a 1:1 ratio of weak acid: conjugate base. Make up two beakers containing such a solution.

2. Take the pH of these two solutions (Thought question for your notebook: what do you expect this pH to be? how close are you?).

3. In the presence of your instructor, add a pipette full of 0.1 M HCl to one of the beakers and observe the pH. Notebook: Does this change in pH meet your expectations for a good buffer?

4. Repeat step 3 with ~0.1 M NaOH.

B. Using Other Reagents
The following reagents will be available in the laboratory:

<table>
<thead>
<tr>
<th>Solids</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium acetate (trihydrate); FW 136.08 (pKₐ = 9.25)</td>
<td>NaOH (from Week 1)</td>
</tr>
<tr>
<td>ammonium chloride; FW 53.5 (pKₐ = 9.25)</td>
<td>0.10 M HCl</td>
</tr>
</tbody>
</table>

Your goal is to prepare a buffer that will buffer against pH changes at both the following pH values (one partner does one pH, another does the other):

- pH 9
- pH 5

Possible helpful information for your task:

- A 0.200 M solution should have a reasonable buffering capacity.
- 100 mL volumetric flasks will be conveniently available for your use.
- Formula weights are the same as molecular masses but are unit-less (that is, the grams per mole is understood).
- If you have a weak acid, you can conveniently obtain its conjugate base by adding strong base.
- If you have a weak base, you can conveniently obtain its conjugate acid by adding strong acid.
- The pH you chose for your buffer should correspond with the pKₐ of the reagent you are also choosing to use.

After you have created a buffer solution that you believe will act as a good buffer at either pH 5 or pH 9, set up two ~50 mL aliquots in separate beakers. Take the pH of each aliquot and record its value, then ask your instructor to add acid and base to your buffer and record the new pH values. If you constructed an effective buffer, then the pH change should be small in each case.
**Record all of your experimental observations in your laboratory notebook. Your notebook should include:**

1. The concentration and uncertainty in your NaOH stock solution
2. pH calibration details
3. Unknown weak acid titrations
4. pKa and formula weight or your unknown weak acid
5. Identity of your weak acid
6. Buffer tests A, B, and C
7. Buffer data analysis described in step D.
8. Details on the preparation and performance of the pH 5 or 9 buffer.