Experiment 9: WEAK ACID IONIZATION
CONSTANT & PROPERTIES OF A BUFFERED SOLUTION

Purpose:
Part I: The acid ionization constant of a weak acid is to be determined, and the acid is identified accordingly.
Part II: The effect of adding acid and base to a buffered solution is to be examined.

Introduction: The pH of a solution is defined by the following equation:

\[ \text{pH} = -\log[H^+] \]
\[ \text{or} \]
\[ \text{pH} = -\log[H_3O^+] \]

The pH of a solution tells us the acidity (or basicity) of the solution. It is a convenient way of expressing the concentration of the hydrogen ion, H\(^+\), or hydronium ion, H\(_3\)O\(^+\), in aqueous solutions. For example, instead of saying that a solution contains 0.0001 M H\(_3\)O\(^+\), we can simply say that it has a pH of 4.

One can measure the pH of a solution experimentally in two ways. The first method utilizes chemicals called INDICATORS, which are sensitive to pH. These substances have colors that change over a relatively short pH range (about 2 pH units) and can, when chosen properly, be used to roughly determine the pH of a solution. Two very common indicators are litmus, usually used on paper, and phenolphthalein, the most common indicator in acid-base titrations.

The other method for finding pH is with a pH meter. In this device, two electrodes (or a single “combination” electrode) are immersed in a solution. One electrode is sensitive to [H\(^+\)] and the potential between the two electrodes is related to the pH. The pH meter is designed so that the scale will directly furnish the pH of the solution. It gives much more precise measurement of pH than does a typical indicator, and is ordinarily used when an accurate determination of pH is needed.

Some acids and bases undergo substantial ionization in water, and referred to as being strong because of their essentially complete ionization in reasonably dilute solutions. Other acids and bases, because of incomplete ionization (often about 1% ionized in 0.1 M solution), are called weak. Hydrochloric acid, HCl, and sodium hydroxide, NaOH, are typical examples of a strong acid and a strong base respectively. Acetic acid, HC\(_2\)H\(_3\)O\(_2\), sometimes abbreviated HOAc, and aqueous ammonia, NH\(_3\)(aq), are classic examples of a weak acid and a weak base.

A weak acid will ionize according to the Law of Chemical Equilibrium:

\[ \text{HA} (aq) \rightleftharpoons H^+ (aq) + A^- (aq) \]
\[ \text{or} \]
\[ \text{HA} (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq) + A^- (aq) \]
At equilibrium, \[ K_a = \frac{[H^+][A^-]}{[HA]} \]  
or \[ K_a = \frac{[H_3O^+][A^-]}{[HA]} \]  

\( K_a \) is referred to as the acid ionization constant, and is characteristic of the acid. A similar relation can be written for the solutions of a weak base.

**DETERMINATION OF K\(_a\) OF A WEAK ACID**

The value of \( K_a \) for a weak acid can be found experimentally in several ways. Perhaps the most obvious way is to simply measure the pH of a solution of the acid of known molarity by setting up an ICE table. The [H\(^+\)] at equilibrium can be calculated from the pH, using Equation 1. According to the stoichiometry shown in Equation 2, we see that [H\(^+\)] must equal to [A\(^-\)], since there is no other source of H\(^+\) but from HA. To obtain the [HA] at equilibrium in Equation 3 we subtract [H\(^+\)] from the initial [HA] to correct for the amount of HA lost by the dissociation. By substituting [H\(^+\)], [A\(^-\)], and [HA] equilibrium values into Equation 3, \( K_a \) can be calculated.

\[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \]

I \hspace{1cm} \text{initial [HA]} \hspace{1cm} 0 \hspace{1cm} 0

C \hspace{1cm} -x \hspace{1cm} +x \hspace{1cm} +x

E \hspace{1cm} \text{initial [HA]} \hspace{1cm} -x \hspace{1cm} x \hspace{1cm} x

where \( x = [H^+] \) which can be determined from pH measurements

Another very simple procedure, which involves very little calculation, is accurate and does not even require the knowledge of the molarity of the acid. A sample of a weak acid, often a solid, is dissolved in water. The solution is divided into two equal parts by volume (Soln 1 and Soln 2), each containing the same molar concentration of HA. With the same volume of solution involved, each has the same number of moles of HA as well.

Soln 1 is titrated to a phenolphthalein end point with NaOH, and all of its HA is converted to A\(^-\) by the reaction:

\[ \text{OH}^- (aq) + \text{HA} (aq) \rightarrow \text{A}^- (aq) + \text{H}_2\text{O} (l) \]  
Equation 4

The number of moles of A\(^-\) produced equals the number of moles of HA that was in Soln 1 because its stoichiometric ratio is 1:1. It is also equal to the number of moles of HA in Soln 2. The two solutions are then mixed, and the pH of the resultant solution is recorded. In this resultant solution because [HA] equals [A\(^-\)], these two terms in Equation 3 cancel out, leaving us with simply [H\(^+\)] = \( K_a \).
EXPERIMENT 9: WEAK ACID Ka & PROPERTIES OF BUFFER SOLUTION

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

\[ K_a = [H^+] \quad \text{Equation 5} \]

By finding the log of both sides of the equation, and then multiplying both sides by \(-1\), we see that \( pK_a = \text{pH} \).

\[-\log K_a = -\log [H^+] \]
\[ pK_a = \text{pH} \]

The resultant solution described above is sometimes referred to as being “half-neutralized.” Remember that it is prepared by mixing equal volumes of a solution that has been neutralized and a solution that has not. This gives us a solution where \([HA] = [A^-]\) and \( pK_a = \text{pH} \). By measuring the pH of such a solution we would be able to determine its \( pK_a \) and calculate its \( K_a \).

HOW BUFFERS WORK

Buffers are solutions that are remarkably resistant to pH changes despite the addition of an acid or base. Buffers contain approximately equal amounts of a weak acid and the salt of its conjugate base (or a weak base and the salt of its conjugate acid). In this experiment we will be dealing with the former combination (weak acid/conjugate base).

The half-neutralized solution produced in the aforementioned procedure is an example of a buffer solution. The solution contains equal amounts of the weak acid (HA) and the anion (A\(^-\)) present as its salt. If a strong acid is added to the buffer, the H\(^+\) ion from the strong acid is removed by its reaction with the A\(^-\) ion in the buffer, keeping the [H\(^+\)] level about where it was before the addition. Similarly if a strong base is added to the buffer, the OH\(^-\) from the base is removed by its reaction with the HA in the buffer, keeping the [OH\(^-\)] level from increasing. In contrast, if similar amounts of a strong acid or base were added to an unbuffered sample (such as plain water) the pH could easily change by several pH units.

HANDLING SIGNIFICANT FIGURES IN pH ↔ [H\(^+\)] CONVERSIONS

- The number of **decimal places** in the pH determines the number of **significant figures** in the corresponding [H\(^+\)].
  
e.g.  pH = 2.35 has two decimal places, so [H\(^+\)] = 4.5x10\(^{-3}\) M (2 sig.fig.)
  
  pH = 8 has no decimal places, so [H\(^+\)] = 10\(^{-8}\) M (no sig. fig.)

- The number of **significant figures** in [H\(^+\)] determines the number of **decimal places** in the corresponding pH.
  
e.g.  [H\(^+\)] = 0.00817 M has 3 significant figures, so pH = 2.088 (3 decimal places)
  
  [H\(^+\)] = 1x10\(^{-2}\) M has one significant figure, so pH = 2.0 (1 decimal place)

Safety Precautions:

Wear your goggles at all times. Avoid contact with the aqueous solutions of NaOH and HCl. Both chemicals are corrosive, can cause burns and irritation to your eyes and lungs.
**Procedure:** Work with one partner

**Part I: Determination of the Dissociation Constant of a Weak Acid, \( K_a \).**

1. Obtain an unknown solid acid sample from your instructor. RECORD the unknown number in your lab notebook.
2. Obtain approximately 40 mL of 1 M NaOH in a clean and dry LABELED beaker. Do NOT waste our NaOH solution!
3. Rinse a buret twice with small portions (~5 mL each) of the 1 M NaOH solution. Remember to get rid of the air bubble at the tip of the buret. Fill the buret to the 25.00 mL mark with 1 M NaOH.
4. Using a 50-mL graduated cylinder measure out 50.0 mL of deionized water and pour it into a clean and dry 250-mL Erlenmeyer flask. Dissolve about half of your unknown solid acid sample in the water and stir thoroughly with a glass stirring rod.
5. After you are sure all of the unknown solid acid has dissolved, pour the entire solution into the 50-mL graduated cylinder. Transfer exactly half of this solution back into the 250-mL Erlenmeyer flask. Gently slide a magnetic stir bar into the flask.
6. Add 2-3 drops of phenolphthalein indicator to the solution in the flask and titrate the solution to a faint pink endpoint using the 1 M NaOH in the buret. (Volume readings do not have to be taken here). Add the hydroxide solution slowly while the content of the flask is being stirred. As the end point approaches, add the solution drop by drop until the solution has a permanent, light pink color that persists for 30 seconds. You can split drops by allowing the drop of NaOH solution to build on the buret tip and then washing it into the flask with deionized water.
7. Add the remaining part of the solution from the 50-mL graduated cylinder to the flask containing the neutralized acid and stir to mix.
8. Follow directions in Appendix 4 on the use of the pH meter. In particular read page A-11 on the care of electrodes. Calibrate the pH meter with the pH 7 Buffer Solution as instructed in Step 3 of Appendix 4 (page A-12), and then with pH 4 Buffer Solution in Step 8 of Appendix 4 (page A-13). Finally record the pH of the half-neutralized solution from Step 7 above.
9. For the first trial (only), discard the solution and repeat the determination starting at Step 3 with the other half of your solid weak acid. **For the second trial, do NOT discard the half-neutralized solution. It will be used as a buffer in Part II.**

**CALCULATIONS:** Write neatly on your own paper. Perform calculations individually. **DO NOT COPY FROM YOUR PARTNER.**

For each trial, calculate the \([H^+]\) from the observed pH and state the \( K_a \) of your unknown acid. Calculate the average \( K_a \) from the two trials. Design a table to summarize your results. Below are the literature values for the equilibrium constant of possible acids. Based on your results, which is your unknown acid?

<table>
<thead>
<tr>
<th>Acid</th>
<th>d,l-mandelic acid</th>
<th>chloroacetic acid</th>
<th>sodium bisulfite</th>
<th>sodium bisulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_a )</td>
<td>( 4.3 \times 10^{-4} )</td>
<td>( 1.3 \times 10^{-3} )</td>
<td>( 1 \times 10^{-7} )</td>
<td>1.2 x 10^-2</td>
</tr>
</tbody>
</table>

Next, calculate the percent difference in \( pK_a \) between the two trials and the % error in your average \( pK_a \). Watch your significant figures at all steps of your calculations.
Part II. Properties of a Buffered Solution

In this part of the experiment, note that you will be using 0.1 M and not 1 M NaOH.

10. Copy the pH of the second buffer (half-neutralized) solution from Part I (Step 8) into your data table for Part II. Measure out 25 mL of this second buffer from Part I into a small beaker, add 10 drops of 0.1 M NaOH and mix thoroughly. Record the pH of the solution in your lab notebook.

11. To another 25 mL of your second buffer solution from Part I, add 10 drops of 0.1 M HCl, mix thoroughly, and record the pH of the mixed solution in your lab notebook.

12. Measure the pH of 50 mL of tap water. If the pH measured is not between 5.0 to 8.0, discuss your result with your instructor before continuing with the experiment. (Obviously you should be rinsing your pH electrode between test samples.)

13. To another 25 mL sample of tap water add 10 drops of 0.1 M NaOH. After mixing, record the pH.

14. To yet another 25 mL sample of tap water, add 10 drops of 0.1 M HCl. After mixing, record the pH.

15. CLEAN-UP: The solutions may be discarded in the sink because they are just weak acid, weak base or salt solutions.

CALCULATIONS: Write neatly on your own paper. DO NOT COPY FROM PARTNER.

- Calculate the changes in pH (Δ pH) for the buffer due to (a) adding the aqueous NaOH, and (b) adding the aqueous HCl. Show your calculations.

\[ Δ \text{pH} = \text{new pH} - \text{original pH} \]

- Calculate the Δ pH for tap water due to (a) adding the aqueous NaOH, and (b) adding the aqueous HCl. Show your calculations.

- Design a table to summarize your results.

Data Tables for the lab notebook: This experiment is simple enough that you should be able to prepare your own. Be sure to do this before you arrive to the prelab.

Preparation for Pre-Lab Quiz:

1. How is the pH electrode (or pH probe) to be rinsed with deionized water?

2. After the pH probe has been rinsed with deionized water it has to be dried before being immersed in the sample to be analyzed. What is the proper technique of drying the electrode?

3. At the end of experiment how is the pH probe to be stored in order to keep it from drying out?

4. A solution of NaCN has a pH of 9.5. Find the [H\(^+\)] in the solution. Is the solution acidic or basic?

5. A 0.100 M solution of the weak acid HB has a pH of 3.00. What are the [H\(^+\)], [B\(^-\)], and K\(_a\) for this acid?

6. A solid acid is dissolved in water. Half the solution is titrated to a phenolphthalein end point with NaOH solution. The neutralized and acid solutions are then mixed and the pH of the resulting solution is found to be 4.60. Find K\(_a\) of the solid acid.

7. Assuming your buffered solution contains acetic acid, HOAc, and the sodium salt of its conjugate base, NaOAc. Show the net ionic equations that occur when this buffered solution reacts with: (a) added strong acid, H\(^+\), or (b) added strong base, OH\(^-\).
Post-Lab Questions:

1. In Part I, you were to use half of the solid unknown weak acid for each trial. Does it matter if you did not use EXACTLY half and therefore had different amounts of the solid acid for each trial? Would it increase, decrease or have no effect on the acid ionization constant you are reporting? Explain.

2. Biochemists and biologists often use the Henderson-Hasselbalch equation in working with buffers:

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

\[ \text{HA} + \text{NaOH} \rightleftharpoons \text{H}_2\text{O} + \text{Na}^+ \text{A}^- \]

When an acid solution is half-neutralized, half of the HA has been converted to A\(^-\), and half of it is still in the form of HA. Therefore [HA] = [A\(^-\)]. What happens to the Henderson-Hasselbalch equation when [HA] equals [A\(^-\)]? How is it simplified?

3. The Henderson-Hasselbalch equation is merely a shortcut to working through the ICE table. If the acid is a strong acid, what would the ICE table look like for a 1M HA solution? Complete the ICE table below for a strong acid.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1M</td>
<td>?</td>
</tr>
<tr>
<td>C</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>E</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

What would the K\(_a\) expression look like based on the ICE table? Explain.

4. In Part II, what reaction is taking place when aqueous NaOH is added to a buffer so that the pH does not increase? What reaction is taking place when aqueous HCl is added to a buffer so that the pH does not decrease? Answer in full sentences and also write net ionic equations to illustrate your answers. In your answer do not use the generic formulas, HA and A\(^-\). Use the actual formula of your unknown acid.

5. The purpose of Part II was to show how addition of a strong acid and of a strong base does not significantly affect the pH of a buffer. What role does the tap water play? Explain fully.

Special Instructions for the Formal Lab Report:

How well you follow the format described in Appendix 6 will account for 25% of the grade. The accuracy of your measurements, how well you design your tables and develop the paragraphs of your introduction, discussion and conclusion will account for 50% of the grade. The remaining 25% will be based on how well you answer the post-lab questions. Review Appendices 6 and 7 on what should be in the formal lab report. There are no Calculations & Results Pages provided for this experiment. You must design your own. Present all data and results in a table format. You will be graded on how well you design these tables for comparison of values. Refer to previous experiments as guideline as to how tables are set up. Write separate discussions, error analyses and conclusions for Part I and II.

In Part I, be sure to state your unknown number and the identity of your unknown acid in your discussion and conclusion. Discuss whether your results are reliable. What is the purpose of calculating the percent difference and of the percent error? In Part II, first explain what a buffer is and then discuss how the ΔpH values you have calculated illustrate the effectiveness of your buffer.