Lab 4: Designing and Preparing a Buffer

The dissociation of a weak acid in water yields H⁺ ion and the conjugate base of the acid, where the extent of dissociation is defined by the acid equilibrium constant, Ka:

\[ \text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq) \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]

The anion (A⁻) in the above reaction, referred to as the conjugate base of HA, gives rise to the following equilibrium when an ionic salt (i.e. NaA) of this ion is dissolved in water:

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

Note that the anion accepts H⁺ from water, thereby acting as a base in this equation, consistent with its name: conjugate base.

When a weak acid is dissolved in a solution containing its conjugate base, the result is a mixture that is highly resistant to change in [H⁺] upon addition of either strong acid or strong base. Added OH⁻ ions consume H⁺ ions already present which are replaced by further dissociation of HA; while added H⁺ ions are consumed as the equilibrium shifts to the left producing more HA. These solutions are known as buffer systems. They are used to control the [H⁺] as is required in a wide variety of practical applications.

In a buffer system [H⁺] is dependent on the ratio of weak acid to conjugate base, as can be seen by rearranging the equilibrium expression as follows:

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

Given that [H⁺] is usually expressed in units of pH (pH = -log [H⁺]), the above equation can be conveniently rewritten by taking (– log) of both sides, and substituting:

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

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

In this lab you will accomplish several tasks:

- You will measure the pH of a series of salts (at least one will donate H⁺ to water, and at least one will accept H⁺ from water) and write net ionic equations consistent with your results.
- You will combine known concentrations and volumes of conjugate base and weak acid and measure the resultant pH, allowing you to use equation (1) to determine Ka of the acid.
- You will compare the effects of adding strong acid and strong base to deionized water with those of similar additions to a buffer solution. You will explore the limitations of a buffer
system by purposely adding sufficient OH\(^-\) ion to convert all HA to A\(^-\) ion thereby eliminating this important component of the buffer.

- Finally you will use equation (3) to design and prepare a buffer of a specific pH.

**Procedure**

Part 1, pH of salt solutions: You will need a calibrated pH meter and 4 clean and dry 50 mL beakers, one containing distilled water to rinse the pH probe. Select 3 clean and dry 50 mL beakers (rinse and dry the beakers to remove residual acid or base from a previous experiment that could affect your pH reading), and label them A, B and C. Solutions of 0.10M NaCl, 0.10M Na\(_2\)CO\(_3\) and 0.10M NaHSO\(_4\) will be provided. Pour a small amount of 0.10M NaCl into beaker A, 0.10M Na\(_2\)CO\(_3\) into beaker B, and 0.10M NaHSO\(_4\) into beaker C. Use a pH meter to measure the pH of each solution, and record each result on your data table. Make sure you immerse the pH meter probe in distilled water between pH measurements. Write an equation to represent the equilibrium reaction which accounts for pH readings of samples with a pH lower than 6 or higher than 8.

Part 2, Calculating Ka from buffer pH, and exploring properties of buffers: You will need a calibrated pH meter and: a glass stir rod, 6 clean, dry 50-150 mL beakers (one with water for rinsing, two to store reactants from the lab cart, one to prepare a 1:1 buffer and a second to split the contents of the buffer into two separate beakers to treat differently, and one to prepare a 1:10 buffer), 1 large beaker to hold test tubes upright, 2 test tubes + 2 disposable pipets with bulb, 5 or 10 mL grad cylinder, and a 2 5 or 50 mL graduated cylinder.

Each of the following solutions (ALL 0.10 M) will be provided: CH\(_3\)COOH, NaCH\(_3\)COO, NH\(_4\)Cl, NH\(_3\), NaHCO\(_3\), and Na\(_2\)CO\(_3\).

Select one buffer system to work with for part 2 of this experiment that you can prepare from two of the provided solutions. Record on your data chart the buffer system you have selected. Pour around 50 mL of each of the two solutions you require into two separate beakers to carry to your bench. Label the beakers, so you know which contains the acid component of your buffer, and which contains the base. Place about 10 mL of 0.10 M NaOH into one test tube, and 5 mL of 0.10 M HCl into another test tube (label the tubes), and bring them to your bench. Store them in a large beaker (to hold them upright) with a disposable pipet and bulb so you will be ready to dispense them when needed.

Use a graduated cylinder to measure 20 mL of the acid component of your buffer into a 150 mL beaker and 20 mL of the base component of your buffer into the same 150 mL beaker. Stir this mixture well using a glass stir rod.

Measure and record (on your data chart) the pH of your buffer. Since the Molarity and volume of both acid and base are identical \([\text{acid}] / [\text{base}] = 1\). Use this information, your pH (converted to \([H^+]\)) and equation (1) to calculate Ka for the acid in your system. Show your calculations in the space provided below the data chart, and record your Ka in the chart.
Measure and record the pH of distilled water by pouring a small amount of distilled water into a clean dry beaker.

Add 30 mL of distilled water to your buffer and stir well. Measure and record the pH (as pH after dilution with water).

Divide your buffer solution into two portions in separate 50 – 100 mL beakers. Add 1-2 mL 0.10M HCl to one of the portions, and 3 mL 0.10M NaOH to the other. Stir each solution and measure and record the pH.

Add 1-2 mL 0.10 M HCl to 30 mL distilled water in a beaker and measure and record the pH.

Add 3 mL 0.10 M NaOH to 30 mL distilled water in a beaker and measure and record the pH.

Rinse and towel dry your beakers.

Prepare a new buffer of the same system only this time use 2 mL of your selected acid, and 20 mL of your selected base. Measure and record the pH.

Calculate Ka for your acid using equation (1). Recall that \([H^+] = 10^{-\text{pH}}\) and according to your prep of this solution \([\text{acid}]/[\text{base}] = .02/.20\). Show your calculation below the data chart, and record the calculated Ka in the chart.

Add 3 mL NaOH to the 2:20 buffer solution and measure and record the pH. Is this pH a much larger change than for the 1:1 buffer solution? Do you know why or why not?

Part 3, Designing and preparing a buffer of a specific pH: You will need a calibrated pH meter, a 25 mL graduated cylinder, a glass stir rod and a clean dry 150 mL beaker.

You will be assigned a specific pH by your instructor which will not be the same as any of your classmates. Record the pH you have been assigned (your “target pH”). Determine which buffer system available would be appropriate to design a buffer of the pH you were assigned. Check with your instructor to make sure you’ve selected the correct system for your target pH before proceeding further.

Calculate the volume of each stock solution you need to prepare 30 – 50 mL buffer solution of your target pH. (Hint, choose either acid or base to begin with 20 mL, and determine the volume you will need of the other solution to have the correct base/acid ratio for your target pH).

Record your calculations. Measure the calculated volume of each solution into a clean dry beaker and check to see that you obtain your target pH. Record the pH you obtain.

Clean up your station, put away all the extra beakers you obtained from the shelves, and refill your distilled water bottle. The materials used in this lab are safe to dispose down the drain.
Data Tables

Part 1: pH of 0.10 M Salt Solutions

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>Na$_2$CO$_3$</th>
<th>NaHSO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For solutions having pH less than 6 or greater than 8 write a NET ionic equation to explain qualitatively why the solution has that pH:

Solution: ___________ equation: _________________________________________

Solution: ___________ equation: __________________________________________

Part 2: Buffer system selected for initial study:______________________________

<table>
<thead>
<tr>
<th>Buffer System</th>
<th>Acid/Base = 1:1</th>
<th>Acid/Base = 1:10</th>
<th>Pure water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed pH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH after dilution with water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH after addition of HCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH after addition of NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated $K_a$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ka calculation:

Part 3: Design of buffer: Target pH __________________
Acid/base system selected ________________ $pK_a$ of acid selected ________
________mL of ___________ + ___________mL of ________

Show calculations:
Lab 4 Post Lab Questions

1.) In part 1 you measured the pH of three salt solutions, and wrote an equation to account for your results. Which of the salts is a weak acid, and what is its conjugate base? Which of the salts is a weak base and what is its conjugate acid?

2.) Compare (providing an explanation!) the effect on pH of strong acid and strong base additions to pure water vs similar additions to your prepared buffer. Was the effect of adding OH\(^{-}\) to the buffer with and acid/base ratio = 1:10 similar to that for adding OH\(^{-}\) to water? Why do you think that is so?

Explain your observation of the effect of dilution (addition of pure water) on pH of your buffer.

3.) Compare experimental and the literature values for Ka of the acid you used in part 2, offering some possible reasons for a difference in values.

4.) The buffer you designed was prepared by using stock solutions of a weak acid and its conjugate base. An alternative way to prepare a buffer is to add strong base to a weak acid, (producing conjugate base and consuming some initial acid). Calculate the volume of 0.10M NaOH you would need to add to 20mL of 0.10 M weak acid in your designed buffer to prepare a buffer of your target pH. Compare this to the volume of conjugate base solution required to form a buffer of the same pH from the same volume and concentration of weak acid. What is the difference in the calculation in these two approaches to preparing a buffer of the same pH?

5.) Were you able to achieve the desired pH? What were some of the difficulties you had during this lab?
Lab 4 Pre-lab Questions:

1.) A chemist prepares a 0.50 M solution of NaF which gives a measured pH of 8.58; and also prepares a 0.50 M solution of NH₄Cl which gives a measured pH of 4.78. Write net ionic equations consistent with each of these observations:

2.) What is the conjugate base of the acid, NH₄⁺? What is the pKa of NH₄⁺?

3.) I prepare a buffer by mixing 20 mL of 0.10 M HOCl with 20 mL of 0.05 M NaOCl, and measure the pH to be 7.15. Using this information calculate (show your calculations) the Ka for hypochlorous acid (HOCl).

4.) You are asked to design three buffers of the following pH values: 9.10, 10.45, and 4.65. You have the following 0.10M solutions available: CH₃COOH, NaCH₃COO, NH₄Cl, NH₃, NaHCO₃, and Na₂CO₃.
Which solution will you choose to design each buffer?
- pH 4.56 ______________________________________________________________________
- pH 9.10 ______________________________________________________________________
- pH 10.45 ______________________________________________________________________

5.) Nitrous acid, HNO₂, has a Ka = 4.5 x 10⁻⁴. A student is asked to prepare a buffer having pH 3.60 using the following solutions: 0.10 M HNO₂ and 0.10 M NaNO₂. How many milliliters of NaNO₂ solution should be added to 20 mL of 0.10 M HNO₂ to make the buffer?