Buffer Capacity

Introduction

Acid/base chemistry, essentially the exchange of a proton, affects much of the chemistry we study. Therefore, an understanding the chemistry of acids and bases is essential. That is why the distinction between strong and weak acids and bases and their reactions was a significant portion of the general chemistry curriculum. One topic discussed in general chemistry was that of buffers. A buffer is defined as a solution that resists changes in pH upon the addition of an acid or base. The behavior of a buffer depends upon the equilibrium of the given acid/base system. In order for a system to behave as a buffer it has to fulfill two criteria:

- A buffer system is comprised of a weak acid and its conjugate base or a weak base and its conjugate acid. Therefore, acetic acid and sodium acetate make a good buffer; but, nitric acid and sodium hydroxide do not.
- The pK$_a$ of the weak acid should be close to the desired pH of the solution. (Or, the pK$_b$ of the weak base should be close to the pOH.)

The second criteria brings us to the topic of this experiment: buffer capacity. Roughly speaking, buffer capacity is the ability of a buffer solution to resist a change in pH.

Buffer capacity is measured as the amount of acid/base it takes the change the solution by one pH unit. Though applicable to basic buffers, the examples used in this handout will all refer to weak acid systems. A buffer works because the equilibrium that exists between the weak acid (HA) and its conjugate base (A$^-$).

\[
HA + H_2O \rightleftharpoons H_3O^+ + A^-
\]  

(1)

The equilibrium constant (K$_a$) for this process can be written in the form of the Henderson-Hasselbalch equation.

\[
pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right)
\]

(2)

The buffer capacity (β) is derived from this same equilibrium. We will cover this derivation in detail during the practicum.
\[ \beta = \frac{dC_A}{d(pH)} = \ln 10 \left\{ \frac{H + K_w}{H + K_a \cdot F \cdot H} \right\} \]  

(3)

In this equation, \( H = 10^{-pH} \), \( K_a \) and \( K_w \) are the acid equilibrium constant and autoprotolysis of water, respectively, and \( F \) is the total (formal) concentration of the buffer. \(^{1-4}\)

In this experiment, you will prepare several different buffer solutions and determine the buffer capacity for each. Part of the data analysis will include a plot of buffer capacity versus pH and will allow you to compare your results with those expected from the equation for the buffer capacity.

**Procedure**

1. **Calibrate the pH Meter.** A lab instructor will demonstrate the use of the Pasco data loggers, their use as a pH meter and how to calibrate them. Using the pH standards provided (pH 4 and pH 7), calibrate your pH meter.

2. **Calibrate a disposable pipette.** Obtain a plastic, disposable pipette and a 5 mL volumetric flask. Carefully, count the number of drops it takes to fill the flask to the fiducial mark. You will use this information to calculate the volume per drop which, in turn, is needed in the calculation of the buffer capacity.

3. **Effects of buffer composition upon buffer capacity.** In this part of the experiment you will make seven buffer solutions (see Table 1) from the stock solutions provided. You will then add acid or base to these solutions and measure the changes in pH that occur.
   a. **Prepare buffer solutions.** At one of the burette stations, fill the left burette with 0.50M acetic acid and the right burette with 0.50M sodium acetate. Using the burettes, add the volumes of acetic acid and sodium acetate given in Table 1 to 100-mL flasks. Then, fill the flasks to the fiducial mark with DI water. The total buffer concentration (measured as total \([\text{OAc}^-] \)) for these solutions is roughly 0.05M.

   *(You use buffer solution 4 twice; see steps b & c)*

<table>
<thead>
<tr>
<th>Buffer</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4*</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAc</td>
<td>9.5</td>
<td>9.0</td>
<td>7.5</td>
<td>5.0</td>
<td>2.5</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>NaAc</td>
<td>0.5</td>
<td>1.0</td>
<td>2.5</td>
<td>5.0</td>
<td>7.5</td>
<td>9.0</td>
<td>9.5</td>
</tr>
</tbody>
</table>

   *(You use buffer solution 4 twice; see steps b & c)*

   b. **Titrate solutions 1 through 4 with 1.0M HCl.** Using a 25-mL volumetric pipette, place 25-mL of solution 1 into a narrow 100-mL beaker. Record the starting pH of solution 1. Add a small stir bar to the solution and turn on the stirring plate (fast enough for a rapid
mix, not so fast as to cause splashing or expose the pH electrode). Add one drop of 1.0M HCl to the buffer, mix for 10s (ONLY), record the pH. Do this 5 more times until a total of six drops have been added to the solution. Rinse the pH electrode with DI water.
Repeat this process with solutions 2 through 4.

c. Titrate solutions 4 through 7 with 1.0M NaOH. Using a 25-mL volumetric pipette, place 25-mL of solution 4 into a narrow 100-mL beaker. Record the starting pH of solution 4. Add a small stir bar to the solution and turn on the stirring plate (fast enough for a rapid mix, not so fast as to cause splashing or expose the pH electrode). Add one drop of 1.0M NaOH to the buffer, mix for 10s (ONLY), record the pH. Do this 5 more times until a total of six drops have been added to the solution. Rinse the pH electrode with DI water.
Repeat this process with solutions 5 through 7.

4. Effects of buffer concentration upon buffer capacity. Using the burettes and stock solutions as before, prepare two more “50:50” buffer solutions – equal volumes of acetic acid and sodium acetate solutions. (Ask a TA or lab instructor to check over your calculations before making the solutions.) Make one solution with a total buffer concentration of 0.10M and a second with a total buffer concentration of 0.25M. (Hint: How do they differ from buffer #4 in Step 3?)

5. Follow the procedure given in Step 3b for the addition of 1.0M HCl to the buffer solutions: add one drop of 1.0M HCl, record the pH, repeat five more times (total of six drops). Clean up your area. Have the instructor grade your lab book.

Pre-lab Questions
1. What is the pH of a 0.0150 M diethylamine solution? Is this acidic or basic?
2. How would you prepare a 0.100 M pH 5.00 buffer based on pentanoic acid?

Practicum Preparation
1. Tabulate your data in MS Word, MS Excel or a program of your choice that delivers a proper table of data.
2. Go to the CRC and run through the ‘Getting Started’ exercise for IGOR PRO. You can find this under the ‘Help’ menu when you launch IGOR PRO.

Lab report
During the practicum, calculate and report the buffer capacity for each of the buffer solutions you titrated (including those in Step 4). Report your results to the class as a whole and record the results from the other lab groups. Calculate the average buffer capacity for each of the solutions and report it in your Results section using a 95% confidence interval. Use IGOR PRO to generate a graph similar to Figure 1 in the article by Russo and Hanania and include it in the Results section of your lab report. Follow the given outline for lab reports given in the syllabus.
Extra Credit (20 points)

Use IGOR PRO to generate a graph similar to that shown in Figure 2 from the article by Russo and Hanania. In this graph, show the class results for the buffer capacities (use 95% confidence intervals as your error bars) and the theoretical curve for buffer capacity given by equation 3 using an acetic acid/sodium acetate buffer with a total concentration of 0.05M. Include this graph with your lab report.

References