Objectives

You will learn how to prepare buffer solutions. In addition, you will reinforce your understanding of acid-base equilibria and investigate the nature of buffer solutions using titration curves.

Skills

- Interpret the description of a buffer in order to make the correct solution from reagents.
- Calculate the volume of a weak acid and the mass of conjugate base salt needed to make a buffer with a specific pH. This is a special type of solution, which is prepared similarly to solution preparation that you have practiced.
- Prepare a buffer from an acid and its conjugate base components.
- Titrate buffers with a strong acid and a strong base.
- Investigate the nature of buffer solutions with respect to pH, buffer region, and buffer capacity when strong acids and strong bases are added.
- Define what is meant by buffer capacity and interpret when that capacity is exceeded.

Introduction

A buffer is a solution that resists changes in pH when an acid or a base is added. Buffers contain significant amounts of both forms of a Bronsted-Lowry weak acid-base conjugate pair. For example, a solution of 0.100 M HF (a weak acid) and 0.100 M NaF would be a buffer since they are an acid-base conjugate pair.

$$HF_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + F^-_{(aq)} \qquad \text{Equation 1}$$

Upon the addition of an acid such as HCl, the fluoride ion acts as a base to neutralize the added strong acid:

$$F^-_{(aq)} + H_3O^+_{(aq,\,from\,HCl)} \rightarrow HF_{(aq)} + H_2O_{(l)} \qquad \text{Equation 2}$$

The buffer is also able to resist changes in pH if a strong base such as NaOH is added. The conjugate acid (HF) in the buffer is able to neutralize the added strong base:

$$HF_{(aq)} + OH^-_{(aq,\,from\,NaOH)} \rightarrow H_2O_{(l)} + F^-_{(aq)} \qquad \text{Equation 3}$$

You will notice that in both cases where a strong acid or base was added to the buffer mixture, a reaction in the forward direction occurred with one of the components of the buffer, either the acid (Eq. 3) or the conjugate base (Eq. 2). The added strong acid or base upsets the existing equilibrium, and the buffer neutralizes that added acid or base. We are assuming here that the moles of weak acid or weak base in the buffer are greater than the moles of added strong base or acid, respectively. The resulting equilibrium will be moved from its original position since the ratio of the conjugate acid to the conjugate base in the buffer will have changed.

The behavior of buffers is based on the equilibrium between the conjugate acid-base pair shown in the equation (Eq. 1). The resulting equilibrium constant expression is

$$K_a = \frac{[H_3O^+]\,[F^-]}{[HF]} \qquad \text{where } K_a \text{ for HF} = 7.2\text{E-}4 \qquad \text{Equation 4}$$

Upon rearranging this expression, we can see how the hydronium ion concentration depends directly on the value of K_a and on the ratio of the concentrations of conjugate acid and conjugate base in the buffer.

$$[H_3O^+] = K_a\left(\frac{[HF]}{[F^-]}\right) \qquad \text{Equation 5}$$

Since pH = -log $[H_3O^+]$, we can control the pH of a buffer solution by adjusting the ratio of the conjugate acid/base concentrations. Alternatively, if we adjust the pH of a buffer solution, we will be changing the ratio of the conjugate acid/base concentrations. For example, if a small amount of HCl were added to the 0.100 M HF/0.100 M NaF buffer, then the fluoride ion would react to neutralize the added acid (Eq. 2). This reaction will reduce the amount of F^-, and cause a corresponding increase in the number of moles of HF that are present. This in turn will cause a slight increase in the $[H_3O^+]$ concentration. For example, a 1.00 L solution contains 0.100 M HF and 0.100 M F^-. Using Eq. 5,

$[H_3O^+]$ = (7.2E-4) x (0.100 M)/(0.100 M)

So $[H_3O^+]$ = 7.2E-4 M and pH = -log (7.2E-4) = **3.14**

Assume 20.00 mL of 1.00 M HCl is added. A reaction occurs to neutralize the strong acid. Since the volume changed, it is necessary to work with moles in the reaction, and then convert to molarity to perform the equilibrium calculation.

Initial moles HF in buffer = (0.100 M) x (1.00 L) = 0.100 moles HF

Initial moles F^- in buffer = (0.100 M) x (1.00 L) = 0.100 moles F^-

Moles HCl = (1.00 M) x (20.0E-3 L) = 0.0200 moles H_3O^+ added

Table 1 Moles of F^- and HF from HF/F^- buffer and added H^+ from HCl

Reaction	$F^-_{(aq)}$ +	$H_3O^+_{(aq)}$ →	$HF_{(aq)}$ +	$H_2O_{(l)}$
Initial	0.100 moles	0.0	0.100 moles	
Addition		+ 0.0200 moles		
Change	- 0.0200 moles	- 0.0200 moles	+ 0.0200 moles	+ 0.0200 moles
Final	= 0.080 moles	0.0	= 0.120 moles	

Assume the reaction goes to completion with HCl as the limiting reagent. The concentrations of HF and F^- can be calculated based on a total volume of (1.00 L + 20.0E-3 L) = 1.02 L:

$[F^-]$ = (0.080 moles/1.02 L) = 0.078 M. $[HF]$ = (0.120 moles/1.02 L) = 0.118 M

Based on the pH calculation of the re-established equilibrium for the conjugate acid-base pair:

Table 2 Hydrogen fluoride buffer example - ICE Table

Equilibrium	**$HF_{(aq)}$** +	**$H_2O_{(l)}$** ⇌	**$F^-_{(aq)}$** +	**H_3O^+**
Initial	0.118 M		0.078 M	~0
Change	- *x*	- *x*	+ *x*	+ *x*
Equilibrium	0.118 M - *x*		0.078 M + *x*	*x*

With the large amount of products present initially, the value of -x is usually insignificant and thus can be neglected. Enter the numbers back into Equation 5:

$[H_3O^+]$ = (7.2E-4) x (0.118 M)/(0.078 M)

So $[H_3O^+]$ = 1.02E-3 M and pH = -log (1.02E-3) = **2.96**

By taking the negative log of both sides of equation (5) the following "shortcut" formula for buffers is obtained:

$$-\log[H_3O^+] = -log\ K_a - log\left(\frac{[HF]}{[F^-]}\right)$$

OR

$$pH = pK_a + \log\left(\frac{[F^-]}{[HF]}\right) \quad (Henderson - Hasselbalch\ equation) \qquad \text{Equation 6}$$

Buffer range and buffer capacity are terms used to compare the different buffers. Recall that buffers must contain significant amounts of both forms of a Bronsted-Lowry weak acid-base conjugate pair to resist large pH changes: the *buffer range* is the pH region in which this is true. The usual criterion is that the actual concentrations of the conjugate acid and base (ratio of moles of HF to moles of F-) differ by no more than a factor of 10. For example, in a hydrofluoric acid/fluoride solution, this would mean that the ratio of

$[F^-]/[HF]$ should not be greater than 10:1 nor less than 1:10.

The high pH limit of the buffer range for a F^-/HF solution occurs when the ratio $[F^-]/[HF] = 10$.

This pH is easily found by using either equation (5) or Henderson-Hasselbalch Equation (Eq 6).

$$pH = pK_a + \left(\frac{[F^-]}{[HF]}\right) = 3.14 + \log(10) = \mathbf{4.14}$$

Similarly, the low pH limit of the buffer range occurs for a ratio of [F-]/[HF] = 1/10, which corresponds to a pH of 2.14 (using equation (6) as above). Thus, the effective buffer range for fluoride/hydrofluoric acid solution is from pH 2.14 to pH 4.14. Obviously, the center of the buffer range is the pH where the conjugate acid and base forms are equal in concentration, and [F-]/[HF] = 1. When this is true, from equation 5, we see that $[H_3O^+]$ = Ka = 7.2E-4. If we use equation 6 instead, we find that pH = pKa = 3.14. Thus, the buffer range is essentially the pKa +/- 1 pH unit.

There is a limit to how much strong acid or strong base can be neutralized by a buffer before the buffer is overwhelmed and the pH changes rapidly. For example, if enough NaOH is added to our HF/F^- buffer, all of the HF will be converted to F^- through the reaction below:

$$HF_{(aq)} + OH^-_{(aq\ from\ NaOH)} \rightarrow H_2O_{(l)} + F^-_{(aq)} \qquad \text{Equation 7}$$

If the concentrations of the weak acid and conjugate base pair that form the buffer are increased, the buffer will have the ability to neutralize larger amounts of added strong acids and strong bases.

Increasing the concentration increases the *buffer capacity*. The formal definition of buffer capacity is *the moles of added strong acid or strong base that a liter of the buffer can neutralize while still maintaining the pH within the buffer range* (i.e. +/- 1 pH unit). The amount of strong acid or strong base (titrant) that causes the buffers pH to increase or decrease by one pH unit indicates buffer capacity. The buffer capacity is determined by looking at the titration data and the graphed titration curve.

Equipment and Materials

*Sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3\ H_2O$)
*0.600 M Acetic acid (CH_3COOH), $K_a=1.8 \times 10^{-5}$
0.0300 M Imidazole/0.0300 M Imidazolium chloride buffer, $K_a = 1.0 \times 10^{-7}$

0.0300 M Sodium chloride solution		Volumetric pipettes
0.0500 M NaOH	25.00 mL burette	Beakers
0.0500 M HCl	Stir plate	Erlenmeyer flasks
100.0 mL volumetric flask	Stir bar	Pipette bulbs
pH 4, 7, & 10 buffers	pH Meter	Grease pencil or Sharpie

Experimental Procedure

- You will work with your lab partner, a group of two, either Team A (titrate with NaOH) or Team B (titrate with HCl). Students will need both sets of data.

Team A (NaOH Titrations)

- Prepare 100.0 mL of 0.030 M acetate ion/0.030M acetic acid buffer solution.
- Complete three titrations with sodium hydroxide.
- Share your data with your partner team/group.
- Each student will use the titration data to construct one graph.

Team B (HCl Titrations)

- Prepare 100.0 mL of 0.030 M acetate ion/0.030M acetic acid buffer solution.
- Complete three titrations with hydrochloric acid.
- Share your data with your partner team/group.
- Each student will use the titration data to construct one graph.

Three Solutions

- 0.030 M acetate ion/0.030 M acetic acid **buffer**
- 0.030 M imidazole/0.030 M imidazolium chloride **buffer**
- 0.030 M sodium chloride solution

Buffer Preparation -Both Team A and Team B

Prepare 100.0 mL of a buffer containing 0.030 M acetate ion/0.030 M acetic acid. *You will need to calculate the correct amounts of the two compounds that are needed for the buffer.

1. Make the buffer by adding the solid salt component, sodium acetate trihydrate, of the buffer to an empty 100.0 mL volumetric flask. Be sure to measure the mass close to the calculated amount of salt needed. Accurately record the reagent name and the exact amount weighed along with units (at the top of page 11).
2. Add about 40 mL of deionized water to the flask to dissolve the solid. Mix the solution by swirling the flask.
3. Pipet the proper amount of 0.600 M acetic acid into the same volumetric flask. Record the reagent and the exact volume delivered along with units (at the top of page 11). Ask about the sig. figs. for the pipet used if needed.
4. Gently swirl the solution again.
5. Add DI H_2O to the mark, cap and invert the flask numerous times to be sure it is mixed thoroughly. Be sure that all the solid is fully dissolved before using this solution in further work.
6. Measure the initial pH of the buffer you prepared. Compare it to the pH predicted in the pre-lab calculations. If it is more than 0.25 pH units off, consult with your instructor.

Titration set up

Team A will complete three titrations with 0.0500 M sodium hydroxide. Team B will complete titrations with 0.0500 M hydrochloric acid. Follow the directions to ensure proper use of your lab time.

Use the set up shown (**Figure 1**) for the titration to protect the pH probe and expedite the titration. For all the titrations you will use a beaker rather than an Erlenmeyer flask. This is the same setup as was used in the *Determination of pKa and pKb using acid-base titrations* experiment.

For this investigation, we are interested in trends for the solutions as they are titrated with each titrant, an acid and a base. Since we are not looking at this data quantitatively, we will use 1.0 mL increments of titrants, measured with a burette for expediency (it is not necessary to record the normal precision of the burette).

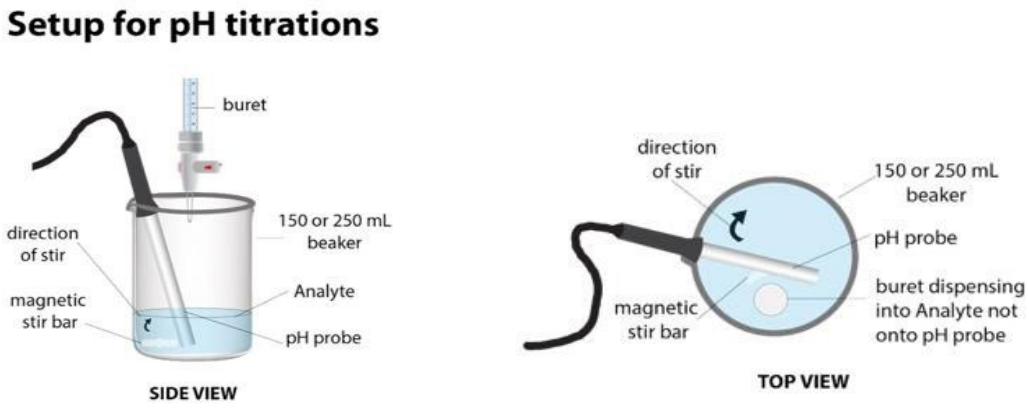

Figure 1 Side View and Top View of the pH Titration set up

Team A Titrations with 0.0500 M Sodium hydroxide

Set up a titration system that has the titrant 0.0500 M NaOH in the burette indicted or labeled for NaOH. You will use the pH meter to monitor and record the pH of the system during the addition of the titrant. Set up the burette so that the titrant is not dripping onto the pH probe. Use a stir bar and stir plate to mix the solution continually while titrating.

Add all titration data into Table 3. Include titles, column/row headings, reagents/solution descriptions, units, and record all data with correct significant figures.

Titration 1: 0.030 M acetate ion/0.030 M acetic acid buffer titrated with 0.0500M NaOH

1. Checking the pH meter: Measure the pH of the pH 7 Buffer (yellow buffer). -
   -If the pH is more than 0.05 off, you need to calibrate the pH meter. The directions to do this are in the lab on a reference sheet – use three buffers – pH 4.01 (pink), pH 7.00 (yellow), and pH 10.01 (blue).
2. Fill the burette with 0.0500 M NaOH. Start the initial volume as close to zero as possible and record the initial volume.
3. Pipet 20.00 mL of the 0.030 M acetate ion/ 0.030 M acetic acid buffer into a 150- or 250-mL beaker. Add about 10.0 mL of DI water to make the volume deep enough to submerge the tip of the pH probe and properly read the pH.
4. Record pH data for the titration in Table 3, starting with the initial pH.
5. Add the titrant in 1.0 mL increments, let the pH stabilize for a few seconds and record the pH value for each volume increment. Continue this titration by adding 1.0 mL of titrant for each volume and pH measurement recorded. Try to get a whole mL added for each increment.
6. Do not stop this titration until you have at least five readings greater than pH 11.0.
7. Do not empty out the burette yet.

Titration 2: 0.030 M imidazole/0.30 M imidazole HCl buffer titrated with 0.0500 M NaOH

1. Refill the burette with 0.0500 M NaOH, record the initial volume and repeat the titration as described in "Titration 1" above using the imidazole buffer as the analyte. Record pH data in Table 3 (new column).
2. Do not stop this titration until you have at least five readings greater than pH 11.0.
3. Do not empty out the burette yet.

Titration 3: 0.030 M sodium chloride titrated with 0.100M NaOH

1. Refill the burette with 0.0500 M NaOH, record the initial volume and repeat the titration as "Titration 1" above using the 0.030 M sodium chloride as the analyte, recording the pH data in Table 3 (new column).
2. Do not stop this titration until you have at least five readings greater than pH 11.0.

Team B Titrations with 0.0500 M Hydrochloric acid

Set up a titration system that has the titrant 0.0500 M HCl in the burette indicted or labeled for HCl. You will use the pH meter to monitor and record the pH of the system during the addition of the titrant. Set up the burette so that the titrant is not dripping onto the pH probe. Use a stir bar and stir plate to mix the solution continually while titrating.

Add titration data to Table 4. Include titles, column/row headings, reagents/solution descriptions, units, and record all data with correct significant figures.

Titration 4: 0.030 M acetate ion/0.030 M acetic acid buffer titrated with 0.0500 M HCl

1. Fill the burette with 0.0500 M HCl. Start the initial volume as close to zero as possible and record the initial volume.
2. Pipet 20.00 mL of the 0.030 M acetate ion/0.030 M acetic acid buffer into a 150- or 250-mL beaker. Add about 10.0 mL of DI water to make the volume deep enough to submerge the tip of the pH probe and properly read the pH.
3. Record pH data for the titration in Table 4, starting with the initial pH.
4. Add the titrant in 1.0-mL increments, let the pH stabilize for a few seconds and record the pH value for each volume increment. Continue this titration by adding 1.0 mL of titrant for each volume and pH measurement recorded.
5. Do not stop this titration until you have at least five readings lower than pH 3.0.
6. Do not empty out the burette yet.

Titration 5: 0.030 M imidazole/0.30 M imidazole HCl buffer titrated with 0.0500M HCl

1. Refill the burette with 0.0500 M HCl, record the initial volume and repeat the titration as "Titration 4" above using the imidazole buffer as the analyte. Record pH data in Table 4.

2. Do not stop this titration until you have at least five readings lower than pH 3.0.
3. Do not empty out the burette yet.

Titration 6: 0.030 M sodium chloride titrated with 0.0.500M HCl

1. Refill the burette with 0.0500 M HCl, record the initial volume and repeat the titration as "Titration 4" above using the 0.030 M sodium chloride solution as the analyte; recording the pH data in Table 4.
2. Do not stop this titration until you have at least five readings lower than pH 3.0.

C. Clean Up

All students automatically receive five "Clean up - Courtesy points" for cleaning up their glassware, equipment, bench and the common area assigned by their instructor. Students that do not check their bin, fill the DI water, or clean-up will have the five points or partial points deducted in the "General Feedback" item in the grading section. If the common areas of the lab are noticeably messy after the lab section is finished, the whole class may be docked these points or partial points.

1. All solutions can be poured in the sink with running water.
2. Use hot soapy water to wash all glassware and appropriate equipment. Rinse well with hot tap water.
3. DI rinse all washed glassware and equipment.
4. Fill the DI water bottle that is at your lab bench.
5. Return equipment to the side bench or bin/drawer depending on where you got it. Let it air dry.
6. Check the bin/drawer at your station and make sure all of the items were returned to it. If materials are missing, let your instructor know so that they can be replaced before the next class.
7. Clean the common area assigned to you by your instructor.
8. Return your personal items to your pack/bag.
9. Clean spills on the balance with the brush, then spray disinfectant onto a paper towel to clean the touch pad and guards on the balance - do not spray the balance directly with disinfectant.
10. Disinfect your work area – areas that cannot be washed in the sink – with disinfectant spray.
11. Wash your hands before you leave the lab.

D. Prepare a Graph

The instructor will assign a team A and Team B to share their data with each other. Each student will graph the six titrations that were performed. Place the data for all six titrations on one graph.

1. This graph must be done by hand.

2. Plot pH (y-axis) versus volume of titrant added (x-axis). Note the volume of titrant is the measured volume at each pH reading. Use the graph guidelines you learned in CHM 115, see Appendix C.
3. Be sure to use different shaped markers (Δ, x, -, □, ●, ○, etc.) or different colors of pen/pencils for the points of each titration (solution and titrant must be listed on the legend).
4. Make a smooth curve for each titration. A smooth curve does not connect the points dot to dot.
5. Include a legend with the correct name for each solution studied.
6. Make sure your graph has a descriptive title and complete axes labels including necessary units.

Data and Report:

Use the worksheet to record your data, create your graph and answer the discussion questions. You will turn the pages in to your instructor.

Be sure to review data table and graph criteria in Appendix C before submitting your work.

Note: You will only have data for three titrations with one titrant – Table 3 or Table 4. Your data table will be graded based on the Tables and Graphs rubric in the reference section at the top of the Labflow manual – Appendix C. Your hand created graph will also be graded with the criteria found in that appendix. You will upload a photo of the data your partners team shared with you.