

## EXPERIMENT 2

### pH Measurements and Buffers

Key Experimental Concepts: Effects of acids, bases, buffers, and other ions on pH.

Analysis Goals: Properly use a pH meter. Use Python coding for repetitive calculations.

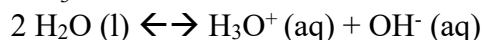
#### INTRODUCTION

This lab allows you to investigate the effects of strong and weak acids and bases, salts, and buffer solutions on solution pH.

The following concepts should already be familiar to you, but here is a brief review.

- According to the Bronsted-Lowry definition, acids are proton donors and bases are proton acceptors. We know that the species primarily responsible for acid behavior in aqueous solution is the hydronium ion,  $\text{H}_3\text{O}^+$ . Basic properties are largely associated with hydroxide ions ( $\text{OH}^-$ ).

- Most acid/base behavior occurs in aqueous solution. Water is *amphoteric* since it can function as either an acid or a base (i.e., it can donate or accept protons). It undergoes autodissociation to form  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions.



The extent of dissociation of water is very small; hence pure water is an insulator, not a conductor of electricity. The equilibrium constant for the above reaction (the “ion product” of water) is only  $1 \times 10^{-14}$  at 25 °C.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$$

The brackets denote the concentration of the indicated ionic species in moles/liter of solution.

- The above equilibrium condition must be satisfied for all aqueous solutions. In pure distilled water that is not in contact with air, the concentration of the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions are equal

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7}$$

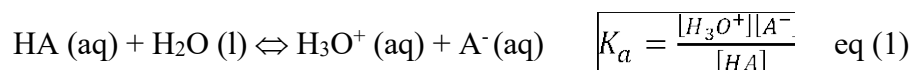
- In acidic solutions,  $\text{H}_3\text{O}^+$  ions predominate,  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ ; in basic solutions,  $\text{OH}^-$  ions predominate,  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ .

- Acidic strength is frequently expressed as pH, defined as

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

In neutral solutions,  $\text{pH} = 7.0$ ; in acidic solutions  $\text{pH} < 7$ ; and in basic solutions  $\text{pH} > 7$ . The lower the pH, the more acidic the solution.

- **Strong acids**, such as HCl, and strong bases such as NaOH are completely dissociated into their constituent ions in aqueous solution.
- **Weak acids** are only partially dissociated or ionized. This means that an equilibrium is established between the dissociated and undissociated forms:



Here HA is the weak acid and A<sup>-</sup> is its conjugate weak base. The equilibrium constant for the dissociation of a HA in water is referred to as K<sub>a</sub>. Note that pK<sub>a</sub> is defined in a way comparable to pH, i.e. pK<sub>a</sub> = - log K<sub>a</sub>. Once you have solved this equilibrium, you can calculate the % dissociation using

$$\% \text{ dissociation} = 100 * [A^-] / [\text{Total weak acid conc.}]$$

- **Weak bases** react with water to achieve equilibrium in which there is an excess of OH<sup>-</sup> ions.



Here B is the weak base and BH<sup>+</sup> is its conjugate weak acid. The equilibrium constant for the dissociation of a B in water is referred to as K<sub>b</sub>. This value can be derived from the K<sub>a</sub> value of the conjugate acid (which may be easier to find) using

$$K_b = 1 \times 10^{-14} / K_a$$

For weak bases,

$$\% \text{ dissociation} = 100 * [BH^+] / [\text{Total weak base conc.}]$$

- **Amphiprotic** describes a substance that can both accept and donate a proton or H<sup>+</sup>. An amphiprotic molecule has characteristics of both an acid and a base and can act as either. Hence it will be involved in two equilibria simultaneously, controlled by a K<sub>a1</sub> and K<sub>a2</sub>. The pH of an amphiprotic substance can be estimated by using both values. See page 218 Harris 9<sup>th</sup> edition (page 224 Harris 10<sup>th</sup> edition) for the simplified pH calculation for intermediate species.
- A buffer is a solution of a weak acid and its conjugate weak base. The equilibrium conditions given by equations (1) and (2) both hold in these solutions, though it is generally more convenient to use the version represented by (1) in calculations. Buffers are formulated so that change in pH on the addition of H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup> is minimized. This is because the weak base, A<sup>-</sup>, will react with added H<sub>3</sub>O<sup>+</sup> and the weak acid, HA, will react with added OH<sup>-</sup>. The equilibrium conditions represented by K<sub>a</sub> continue to be satisfied. The Henderson-Hasselbalch equation is an approximated form of the K<sub>a</sub> expression that is typically used for buffer calculations. If the ratio on the right stays between 0.1 and 10, it is reasonably accurate. Outside of this range, you're better off using eq (1).

$$pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \quad (3)$$

- To summarize, the pH of a weak acid buffer solution is dependent on the pK<sub>a</sub> of the acid and the ratio of conjugate base to acid in a solution. Buffer solutions and acid / base calculations are described in detail in your General Chemistry text and in Harris (Ch. 9.1-9.5 and 10.1-10.4). **Be sure to read these sections in depth!**
- In the first part of this experiment you will measure the pH of aqueous solutions of common chemicals; in the second part you will make some buffer solutions and study their properties.

**PRE-LAB ASSIGNMENT (DUE IN ELN SUNDAY AT 11:59 PM)**

1. Label each of the following solutions as either strong acid (sa), weak acid (wa), strong base (sb), weak base (wb), amphoteric (pp) or neutral salt (n)
2. Calculate the pH of 250 mL of each of the solutions listed. Show work – you can upload a photo of your all your pH calculations into the ELN prelab page if you like.

Substance	Identity	Calculated pH
a. DI Water		
b. 0.05 M NaCl		
c. 0.05 M HCl		
d. 0.05 M HCl in 0.05 M NaCl		
e. 0.05 M Acetic Acid		
f. 0.05 M Sodium Acetate		
g. 0.05 M $\text{KH}_2\text{PO}_4$		
h. 0.05 M TrisHCl		
i. 0.05 M $\text{Na}_2\text{CO}_3$		

3. Calculate the expected pH of the following mixtures described below.
  - (j) 5.0 mL 0.050 M Acetic Acid + 45.0 mL 0.050 M Sodium Acetate
  - (k) 15.0 mL 0.05 M Acetic Acid + 35.0 mL 0.05 M Sodium Acetate
  - (l) 25.0 mL 0.05 M Acetic Acid + 25.0 mL 0.05 M Sodium Acetate
  - (m) 25.0 mL 0.05 M  $\text{KH}_2\text{PO}_4$  + 25.0 mL 0.05 M  $\text{Na}_2\text{HPO}_4$
  - (n) 25.0 mL 0.05 M  $\text{NaHCO}_3$  + 25.0 mL 0.05 M  $\text{Na}_2\text{CO}_3$
4. Note that the total volume of these solutions is 50.0 mL. In lab, you will divide each solution into two 25.0 mL subsamples, and then add a small amount of either strong acid or strong base to each one to see how it responds. To predict the result of such an addition, you'll need to keep track of the stoichiometry of the reaction of the strong acid or base. Let's practice this calculation twice here!



- a. Calculate the pH of **25 mL** of solution (a) following the addition of 1 mL of 0.10 M HCl. (HINT: Start by writing the reaction of HCl reacting with the conjugate base of the buffer solution.)
  - b. Calculate the pH of **25 mL** of solution (a) following the addition of 1 mL of 0.10 M NaOH.
5. Do problems 9-6 and 9-36 in Harris 9<sup>th</sup> edition (9-6 and 9-33 in 10<sup>th</sup> edition).
  6. Prepare your data and observation page in the ELN. Before you come to class your ELN should have a Goal, Safety, Waste and two-column format Procedure written in your own words.

## **EXPERIMENTAL** (work with a lab partner)

### Part 1: Simple Solutions

1. Calibrate a pH meter. See Appendix reference materials in the ELN for details.
2. Transfer 25 mL of each of the solutions listed above to its own labeled 50 mL beaker. Add 1-2 drops of universal indicator to each. Measure the pH with the appropriately calibrated pH meter, being careful to rinse the probe tip after each measurement. How do these values compare with the calculated values from the pre-lab? If there is a common bias, what is the reason for it? (Note: underlined questions in the procedure are to be answered the Data Analysis & Discussion section!)
3. Each lab group will add 1.0 mL of either 0.1 M NaOH or 0.1 M HCl to each of the nine 25 mL solutions. Work things out with the other group at your table so that one group adds acid and the other adds base to their solutions. However, be sure that ALL this data gets recorded in everyone's ELN in a table something like Table 2 shown below.

Example: Solution (a)

	25.0 mL of solution(a) + 1 mL of 0.1 M NaOH. Measure the pH and record the color.		25.0 mL of solution(a) + 1 mL of 0.1 M HCl. Measure the pH and record the color.
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4. Repeat the acid or base addition for solutions e, f, and g **to the respective solutions that have already had acid or base added.** (Leave the “2<sup>nd</sup> HCl” and “2<sup>nd</sup> NaOH” table entries blank for the other solutions.) Once you finish this step you may dispose of your tested solutions in the waste bottle.

Table 2: Measured values of pH and color observations for simple solutions

	Name	Original sol'n	after HCl	after NaOH	after 2 <sup>nd</sup> HCl	after 2 <sup>nd</sup> NaOH
a	DI Water					
b	0.05 M					

	NaCl					
c	0.05 M HCl					
d	Etc.					

### Part 2: Solution Mixtures – Buffers

#### 1. Making buffers

Prepare each of the following solutions (with 3 other students) using graduated cylinders. Add 1-2 drops of universal indicator to each solution. Measure the pH of each solution and observe the colors. Enter all pH data and observations in a summary table in your ELN. **Do not discard these buffer solutions. They are needed for the next part.**

- (j) 5.0 mL 0.050 M Acetic Acid + 45.0 mL 0.050 M Sodium Acetate
- (k) 15.0 mL 0.05 M Acetic Acid + 35.0 mL 0.05 M Sodium Acetate
- (l) 25.0 mL 0.05 M Acetic Acid + 25.0 mL 0.05 M Sodium Acetate
- (m) 25.0 mL 0.05 M  $\text{KH}_2\text{PO}_4$  + 25.0 mL 0.05 M  $\text{Na}_2\text{HPO}_4$
- (n) 25.0 mL 0.05 M  $\text{NaHCO}_3$  + 25.0 mL 0.05 M  $\text{Na}_2\text{CO}_3$

#### 2. Buffers in action

Divide each of the 5 buffer solutions you just made into 25.0 mL portions, each in a separate labeled beaker. (Work things out at your lab table again so that one group adds acid and one group adds base to a set of 5 buffer samples.) To one beaker add 1.0 mL of 0.1 M NaOH and measure the pH that results. To another beaker with the remaining 25.0 mL add 1.0 mL 0.1 M HCl to your buffer solutions and measure the pH. Be sure that everyone records all data, including observations of colors, in their own ELN.

#### 3. Making an acetic acid/acetate buffer at a target pH!

Measure out 15 mL of 0.050 M Acetic Acid and place in a 50 mL beaker. Fill a buret with unstandardized 0.1 M NaOH. Using your pH meter, slowly titrate with the NaOH until a pH of 5 is reached. Record this pH. Determine the volume of NaOH used and the moles of NaOH added. Dilute **precisely** to 25.00 mL final volume with DI water. By diluting *after* the base addition, the final concentration of the total amount of acetic acid and acetate can be easily calculated:  $0.05 \text{ M} \times 15 \text{ mL} / 25 \text{ mL}$ . You have now created a 0.03 M acetic acid / acetate pH 5.0 buffer! Measure and record the pH of the diluted 0.03 M buffer. Did the pH change when you diluted it?

Once you get to this point, you can submit your Data & Obs section, clean up your glassware, chemicals, and benchtop, and get started on working up your data in Python / Jupyter Notebooks.

### Analysis and Results (ELN)

Summarize all results and compare with calculations in properly labeled tables and figures with appropriate narrative (1-2 sentences for each) to explain contents of each summary table and figure. Discussion questions to be considered:

- ☐ How did the pH of each solution compare with your pre-lab (and Python) predictions? (You will want to create some new summary tables for this comparison.) Are a lot of measurements higher or lower than expected? If so, why do you think this is the case?

- ☐ Compare the *changes in pH* and the *final pH* after the acid and base additions. Why do certain solutions end up with extremely high or low pH values (like water did), while others stay closer to the middle (where they started)? HINT: **Discuss specific solutions.** Which solutions started out as buffers? Which became buffers upon addition of acid? Base?
- ☐ Compare the 1<sup>st</sup> vs 2<sup>nd</sup> additions of HCl and NaOH to solutions e-g. Explain the trend.
- ☐ When did taking the activity into account make the biggest difference in pH calculations?
- ☐ Which buffer mixture (j – n) was most effective overall at resisting changes in pH? Which buffer mixture was least effective? Why do you think this is?
- ☐ For the last “target pH” buffer, did the volume of NaOH used match what was expected? How much did the pH change when the solution volume was adjusted to the final volume? Do activity calculations quantitatively explain this change?
- ☐ A pH meter is an instrument that measures a difference in electric potential as H<sup>+</sup> ions bind to a glass membrane. List some conditions (Section 15-5) that can result in error in pH measurement. Do any of them apply to your experiment?