EXPERIMENT I

Acid – Base Equilibrium and Buffers

PURPOSE: Determine the pH of aqueous solutions of weak acids and bases using pH indicators, standardized buffer solutions, and a pH meter. Prepare a buffer of specified pH using a weak acid and the salt of its conjugate base.

INTRODUCTION:

This experiment is related to material covered in lecture last term and to topics being discussed currently. Its goal is to provide practical experience and to provide more meaning to the calculations which you are doing in lecture.

To accomplish this, you will:

- calculate the theoretical pH of a variety of aqueous solutions containing weak acids and weak bases;
- use acid-base indicators to deduce a pH range for each of these solutions;
- determine the pH of an unknown using an acid-base indicator with buffer solutions of known pH;
- learn how to calibrate a pH meter;
- use the pH meter to measure the pH of solutions;
- prepare a buffer with a pH specified by the instructor, using available solutions in the laboratory.

Part 1: pH Calculations

You will be working with 9 solutions, your unknown, and an aqueous sample of your choosing. Before coming to lab, you should calculate the theoretical pH for each of the 9 known solutions as shown in Table 3, using the equilibrium constants given in Table 1, below. <u>Complete calculations should be included in your report for each of the nine solutions.</u>

This portion of the exercise should be completed outside of laboratory and it is certainly appropriate to ask for assistance from your lecture or lab instructor. Although we will be working similar problems in lecture, you may wish to consult the text sections related to "acid-base equilibria" or "weak acids and bases" to complete this part.

The equilibria, equilbrium constants, and pK's provided in Table 1 should be used in these calculations. <u>ALL solutions are 0.100 M.</u> Use the approximation that $0.100 - x \approx 0.100$ to start these calculations. If x turns out to be $<< 0.100$, this is a good assumption and you do not have to use the quadratic formula in your calculations. However, if $x > 0.005$, it would be a good idea to use the quadratic formula to avoid appreciable errors. Indicate in your report which calculations required the use of the quadratic formula.

Table 1

Selected Equilibria

Acetic Acid		
$HC_2H_3O_2 \leftrightarrow H^+ + C_2H_3O_2^-$	$K_a = 1.76x10^{-5}$	$pK_a = 4.75$
Phosphoric Acid		
$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$	$K_{a1} = 7.52x10^{-3}$	$pK_{a1} = 2.12$
$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$	$K_{a2} = 6.23x10^{-8}$	$pK_{a2} = 7.21$
$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$	$K_{a3} = 2.20x10^{-13}$	$pK_{a3} = 12.67$
Ammonia		
$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$	$K_b = 1.79x10^{-5}$	$pK_b = 4.75$

There are essentially 5 situations that you will need to consider.

[1] Weak acid problem

$HA \leftrightarrow H^+ + A^-$ $$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.100 - x)}$$

Examples: 0.100 M $HC_2H_3O_2$ and 0.100 M H_3PO_4

[2] Weak base problem

$B + H_2O \leftrightarrow BH^+ + OH^-$ $$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(x)(x)}{(0.100 - x)}$$

Example: 0.100 M NH_3

[3] Salt of a weak acid

$A^- + H_2O \leftrightarrow HA + OH^-$ $$\frac{K_w}{K_a} = \frac{[HA][OH^-]}{[A^-]} = \frac{(x)(x)}{(0.100 - x)}$$

Example: 0.100 M $NaC_2H_3O_2$ and 0.100 M Na_3PO_4

OR

Salt of a weak base

$BH^+ + H_2O \leftrightarrow B + H_3O^+$ $$\frac{K_w}{K_b} = \frac{[B][H_3O^+]}{[BH^+]} = \frac{(x)(x)}{(0.100 - x)}$$

Example: 0.100 M NH_4Cl

[4] Intermediate salts

Examples: 0.100 M $NaHPO_4$ and 0.100 M Na_2HPO_4

Notice in Table 1 that all of these species are involved in two equilibria. For example, $H_2PO_4^-$ is the "product" of the first equilibrium for phosphoric acid and it is also the "reactant" for the second equilibrium for phosphoric acid. Without going through a fancy, complex derivation, we must consider both situations. It happens that the result is the average of the two equilibria:

$$pH = \frac{pK_1 + pK_2}{2}$$

[5] Salt formed from a weak acid and a weak base

Example: 0.100 M $NH_4C_2H_3O_2$

This can be a complex situation also, but let's look at the two equilibria involved (see Table 1). The ammonium ion is involved in the ammonia equilibrium, which has a $K_b = 1.79x10^{-5}$; the acetate ion is involved in the acetic acid equilibrium, which has a $K_a = 1.76x10^{-5}$. Notice how similar the two values are; however, one is K_b and the other is K_a - essentially representing opposite processes. What is your guess about a compound containing both ions? What is the pH of 0.100 M NH_4Cl and what is the pH of 0.100 M $NaC_2H_3O_2$? Decide what to do with this information.

SAFETY PRECAUTIONS (for all sessions)

> You must wear safety goggles throughout this experiment.

> We will be using solutions of acids and bases throughout this experiment. Their concentrations are all 0.100 M; if there are spills, they can be cleaned by using lots of water.

> Do not rub your eyes unless your hands have been thoroughly rinsed.

> You must wash your hands thoroughly before leaving this lab (and any lab).

Part 2: Determination of pH Range Using Acid-Base Indicators

EQUIPMENT NEEDED

7 small test tubes

Seven acid-base indicators (Table 2) will be used to determine a pH range for each of the 9 solutions, your unknown, and a water sample of your choosing. The colors of the indicators in any solution will define a pH range and should be consistent for all of the indicators used.

For example, if thymol blue is added to a solution and the color is yellow, this indicates that the pH of the solution is in the range 2.8 - 8.0; if bromophenol blue is added to a fresh sample of the same solution and results in a blue color, this indicates that the pH is above 4.6.

Combining both results, we can then say that the only range where both are true is from 4.6 to 8.0; thus, we have narrowed the range. Using the information from all 7 indicators with the same solution often permits us to define a very narrow range for some solutions, but may give us a wide range for others.

PROCEDURE:

[1] In each of the 7 test tubes, squirt an eyedropper full of 0.100 M $HC_2H_3O_2$. The amount does not need to be exact or measured.

[2] Add 2-3 drops of the seven indicators (listed in Table 2), one to each tube. Flick with your finger to mix. Record the **color** of each solution/indicator in Table 3.

[3] Dispose of the contents of the tubes in the sink and rinse; they do NOT have to be dry! Repeat the process for the rest of the 9 solutions, your unknown, and your aqueous sample. Reuse the same test tubes.

RESULTS (to be included in your report)

[1] Determine the pH range for each solution, including your unknown and your aqueous sample, following the method indicated above by using Table 2 for the color ranges of the indicators. Record the value on the bottom of Table 3.

[2] Rank the solutions from most acidic to least acidic according to the pH ranges. Some solutions may be in the same pH range; indicate this as A ~ B ~ C, etc. Are there disagreements between the calculated pH and the experimental pH range? Can you explain these?

[3] How do your experimental results compare to the calculated predictions for the pH of the 9 "known" solutions?

Part 3: Determination of Unknown pH Range Using Buffers and Indicators

EQUIPMENT NEEDED

10 small test tubes

Your unknown has a pH in the range of 6.0 - 8.8. By taking solutions of known pH (such as buffers) in this range, adding an indicator to each, and comparing their colors to that of the unknown with the same indicator, you can narrow the pH estimation of your unknown through visual methods. This is called colorimetry.

Which of the seven available indicators will you use for this trial and how do you decide? (Provide the rationale for your choice in your report.)

You need to be able to differentiate the pH's by differences in color. For example, if you picked bromophenol blue, it has a blue color at all pH values above 4.6, so all of the buffers between 6.0 - 8.8 would be blue (some may be darker than others, but still difficult to differentiate); it would be a poor choice. Before you start this procedure, select the indicator that you want to use and CHECK WITH YOUR INSTRUCTOR to see if you have made an appropriate choice. Be ready to defend your selection.

PROCEDURE

[1] Clean 10 small test tubes; they do not need to be dry. Place a piece of paper beneath the test tube rack so that you can easily label the pH for each tube and the tubes that represent the unknown (and your aqueous sample, if it has a pH in the range of 6.0-8.8).

[2] Using an eyedropper, squirt a dropper full of each of the 8 available buffers to the 8 test tubes. Try to have roughly the same level of liquid in each tube. Add your unknown to the 9^{th} test tube (and your aqueous sample to the 10^{th}, if appropriate) to the same height as the others.

[3] Add 2-3 drops of your selected indicator to each tube; mix by flicking the tube with your finger, and record the color in Table 4. [Your description of the color can be as "artistic" as you wish - as long as you know what it means!]

[4] Compare the color of your unknown /indicator solution with each of the buffers. It might help to do this against a background of white paper or by holding the tubes up to a light or the window. The color may fall in between two known pH solutions; if so, the pH would be estimated to be between those values.

[5] Dispose of the contents of the tubes in the sink and rinse.

Part 4: Determination of Unknown pH Using a pH meter

EQUIPMENT NEEDED

1 pH meter and electrode

1 squirt bottle filled with distilled water

1 beaker to collect the rinse water

PROCEDURE

[1] Your instructor will demonstrate how to calibrate and use a pH meter. There will be beakers of each of the 9 solutions from Procedure {2} on the reagent shelf.

[2] After calibrating the pH meter/ bring a beaker of one solution to your working space and measure the pH; be sure to rinse the electrodes with distilled water between each determination. Record the pH in Table 3. Return the beaker to the reagent shelf and get another solution; repeat the procedure until finished.

[3] Measure the pH of your unknown (pour some into a clean beaker or place the electrode directly into the unknown bottle) and your aqueous sample.

[3] When this portion is completed, rinse the electrode and place it in the storage beaker. Return the meter to its proper location and make sure that it is turned off.

RESULTS (to be included in your report)

[1] Compare the results of the calculated pH, pH range from the indicators (Part 2), and the pH as measured by the meter for the 9 known solutions. Discuss any discrepancies. Which measurement do you feel represents the most accurate results?

[2] In the conclusion of your lab report, you must report one number for the value of the pH of your unknown (and the unknown number). What number will you report, from which determination(s), and why did you decide to report that number?

Part 5: Preparation of a Buffer with a Specific pH

EQUIPMENT NEEDED

1 100-mL beaker

2 100-mL graduated cylinders

4 measuring pipets

pH Meter and Electrode

Your instructor will assign a pH value for which you are to prepare ~ 50 mL of buffer. Once this is prepared, your instructor will measure the pH to see how successful you were in achieving this result.

You may use any of the solutions that are available in lab (all of which are 0.100 M).

It is easiest to use the Henderson-Hasselbalch equation to start:

$pH = pK_a + \log([salt]/[acid])$ [salt] is the concentration of the salt of the conjugate base of the acid being considered. (ex. $NaC_2H_3O_2$ for acetic acid)

OR

$pOH = pK_b + \log([salt]/[base])$ ex. $[NH_4Cl]/[NH_3]$

Let's suppose a student was assigned a pH = 8.00 and wanted to prepare 50.0 mL of final buffer solution.

The first question is which related pair of solutions should be used. The best buffers are made if the pH is close to pK_a (or pOH is close to pK_b).

Looking at Table 1, our desired pH of 8.00 is closest to the pK_a of 7.21, which represents the equilbrium involving $H_2PO_4^-$ (acid) and HPO_4^{2-} (salt), so the Henderson-Hasselbalch equation now becomes

$$pH = pK_a + \log([HPO_4^{2-}]/[H_2PO_4^-])$$

Substitute the numbers, we get

$$8.00 = 7.21 + \log([HPO_4^{2-}]/[H_2PO_4^-])$$

By rearranging, we get

$\log([HPO_4^{2-}]/[H_2PO_4^-]) = 8.00 - 7.21 = 0.79$

> The difference (+0.79) could also be a negative number, depending on the value of pK_a and desired pH. If your number is negative, be sure to carry the minus to the next step.

Take the antilog

$[HPO_4^{2-}]/[H_2PO_4^-] = 10^{0.79} = 6.17$

By cross-multiplying, we get

$[HPO_4^{2-}] = 6.17 * [H_2PO_4^-]$

The job is to prepare 50 mL of a solution that has a concentration of HPO_4^{2-} that is 6.17 times larger than that of $H_2PO_4^-$. Let's approach the problem by asking the question

> How many mL of 0.100 M Na_2HPO_4(*aq*) and 0.100 M NaH_2PO_4(*aq*) need to be combined to make 50 mL of a final solution with $[HPO_4^{2-}] = 6.17 * [H_2PO_4^-]$?

Let x = volume of 0.100 M Na_2HPO_4(*aq*) and y = volume of 0.100 M NaH_2PO_4(*aq*)

Then $x + y = 50$

$[H_2PO_4^-] = (y)(0.100)/50$ From $M_1V_1 = M_2V_2$

$[HPO_4^{2-}] = (x)(0.100)/50 = 6.17(y)(0.100)/50$

Substituting $x = 50 – y$

$(50 – y) = 6.17y$

$y = 7.0$ mL

$x = 50 – 7 = 43$ mL

Now, if you combine 43.0 mL of 0.100 M Na_2HPO_4(*aq*) with 0.100 M NaH_2PO_4(*aq*) the resulting solution should have a pH of 8.00.

Note, if we had equal amounts of the two solutions, the pH would equal $pK_a = 7.21$. We want a higher pH (more basic) and therefore, we are glad to see that we will be adding more of the conjugate base, HPO_4^{2-}, than the acid, $H_2PO_4^-$.

PROCEDURE

[1] Your instructor will assign you a pH value for your buffer. It is __________.

[2] What related pair of solutions will you use to make this buffer? You should be ready to justify your choice (to be included in your report).

[3] Using the method above, calculate the amounts of each solution necessary to prepare 50.0 mL of the buffer. Before actually preparing it, have your instructor look at your calculations (include them in your report)

[4] Using a graduated cylinders, obtain sufficient volumes of your chosen pair to prepare 50 mL of buffer.

[5] Using a separate measuring pipet for each solution, add the appropriate amounts of the two components of the buffer to a clean, dry 100-mL beaker and mix well.

[6] Calibrate a pH meter using the three calibration solutions. Be sure to rinse the electrode with deionized water before testing a solution to prevent cross-contamination.

[7] Using the calibrated pH meter, determine the pH of your buffer and record the result.

[8] If your buffer is at the desired pH, great; you're done. If the pH is slightly high or low, you still have some work to do.

> For too acidic solutions, add 0.1 M NaOH(*aq*) dropwise to your solution, checking the pH with each addition.
>
> For too basic solutions, add 0.1 M HCl(*aq*) dropwise to your solution, checking the pH with each addition.

[9] When you think you are done, take your solution to your instructor, who will measure the pH. If the pH is far from your goal, your instructor may ask you to try a second time for a grade that will be 90% of the maximum grade for the first trial. Your instructor will tell you when to dispose of the solution.

[10] Repeat the procedure for a second pH value.You likely will be using a different set of solutions.

<u>RESULTS</u> to be included in your report)

[1] Was the pH of the solution prepared using Henderson-Hasselbalch? Were they within ± 0.10 pH units of the desired pH? If not, do you have any explanation? Are your calculations correct?
[2] Report your final pH values, and the absolute difference between the target pH and your final values.

REQUIREMENTS for your LAB REPORT

Experiment #1: Acid – Base Equilibrium and Buffers

PURPOSE:

In your words, state the goals of this experiment.

PROCEDURE:

Do not repeat the directions given in the manual. Simply reference them. However, you should mention any changes that were made or any information that was unique to your analysis.

DATA. CHARTS. GRAPHS:

- Table 3
- Table 4
- Initial and final pH values of prepared buffers (procedure 5)

SAMPLE CALCULATIONS:

- Part 1: You need to include the individual pH calculation for each of the 9 solutions

in Table 3.

- Part 5: You need to show your calculation for your buffer preparations.

CONCLUSIONS:

Summary of results, including the answer to your unknown (with unknown number). Answers to questions raised throughout the manual.

Sources of possible or known errors and consequences of those errors (i.e., high results, low results, sporadic results, why?)

OVERALL: (3 points)

Organization of report. Neatness and legibility Grammar and spelling

Table 2

Selected Indicators[(a)]

pH	Thymol blue	Bromphenol blue	Bromcresol green	Bromcresol purple	Bromthymol blue	Cresol red	Phenolphthalein
0	Red	yellow	Yellow	yellow	yellow	red	colorless
1	1.2 - orange	yellow	Yellow	yellow	yellow	orange	colorless
2	orange – 2.8	yellow	Yellow	yellow	yellow	yellow	colorless
3	Yellow	3.0 – green	3.8 – green	yellow	yellow	yellow	colorless
4	Yellow	green – 4.6	Green	yellow	yellow	yellow	colorless
5	Yellow	blue	green – 5.4	5.2 – green	yellow	yellow	colorless
6	Yellow	blue	Blue	green – 6.8	6.0 – green	yellow	colorless
7	Yellow	blue	Blue	purple	green – 7.6	7.0 – orange	colorless
8	8.0 – green	blue	Blue	purple	blue	orange – 8.8	8.2 – pink
9	green – 9.6	blue	Blue	purple	blue	red	pink
10	Blue	blue	Blue	purple	blue	red	10 – magenta
11	Blue	blue	Blue	purple	blue	red	magenta
12	Blue	blue	Blue	purple	blue	red	magenta

(a) Values are from *CRC Handbook of Chemistry and Physics,* Weast, R.C., Ed., CRC Press, Cleveland, OH, pp D-136 to D-137.

(b) See the Zumdahl text, pg 749, for actual color changes.

TABLE 3, pH Measurements

	$HC_2H_3O_2$	$C_2H_3O_2^-$	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	NH_3	NH_4^+	NH_4Ac	unk#	sample
thymol blue											
bromphenol blue											
bromcresol green											
bromcresol purple											
bromthymol blue											
cresol red											
phenolphthalein											
pH range (indicator)											
pH meter											
pH calculation											

TABLE 4 Buffers and pH

Indicator used	
	Color
6.00	
6.40	
6.80	
7.20	
7.60	
8.00	
8.40	
8.80	
Unknown #	**color = pH =**
Aqueous Sample	**color = pH =**