

Acids, Bases, Salts, and Buffers

Goal and Overview

The acidic or basic natures of a number of ions dissolved in aqueous solution will be studied using indicators to approximate pH. An estimate of each ion's acid or base dissociation constant (K_a or K_b) will be calculated and compared to the literature value. The effect of adding strong base to aqueous solutions will be investigated by measuring the pH of solution before and after a small volume of NaOH is added to a weak acid, a weak base, and a buffer.

Objectives and Science Skills

Analyze the colors of different pH indicators to estimate the pH of deionized water and of aqueous solutions containing soluble ionic compounds.

Calculate the approximate K_a or K_b of an ion in solution based on a pH estimate and compare to expected values.

Perform volumetric dilutions and calculate resulting molarities.

Qualitatively and quantitatively analyze and explain the effect of adding strong base to a weak acid, a weak base, and a buffer; explain how a buffer resists changes in pH upon the addition of small amounts of strong base (or acid).

Identify and discuss factors or effects that may contribute to deviations between theoretical and experimental results and formulate optimization strategies.

Suggested Review and External Reading

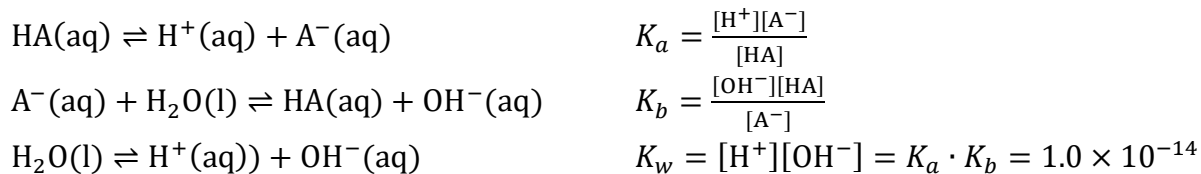
Reference materials and textbook sections on molarity and dilutions, pH, weak acids and bases, soluble salts containing acidic and/or basic ions, and buffers

Introduction

Definitions of an acid include its ability to: 1) generate aqueous hydrogen ions in water, $H^+(aq)$, via a process often described as dissociation; and, 2) act as a proton or H^+ donor. Definitions of a base include its ability to: 1) generate hydroxide ions in water, $OH^-(aq)$, via dissociation or reaction; and, 2) act as a proton or H^+ acceptor.

The strength of an acid or base reflects the extent of its dissociation (and its H^+ donating/accepting power relative to that of water). Strong implies 100% or complete; weak, less than 100%. Acid and base dissociation constants, K_a and K_b , quantify strength (*values provided are at 25 °C*).

A conjugate acid-base pair is comprised of two species that differ by one H^+ , and their relative strengths are related through the water auto-dissociation constant, K_w . As acid strength decreases, conjugate base strength increases (and vice versa).

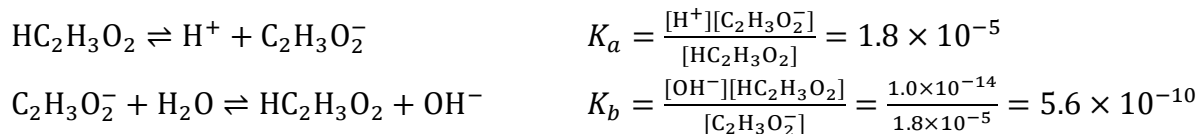


Examples (aqueous solutions; states of matter are omitted)

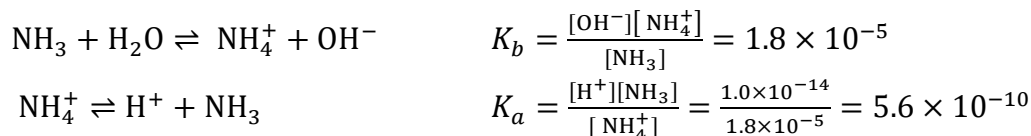
$HCl(aq)$ and $Cl^-(aq)$: HCl is a strong acid. Its conjugate base, Cl^- , is so weak that it is essentially a non-base in aqueous solutions.



$HC_2H_3O_2(aq)$ and $C_2H_3O_2^-(aq)$: $HC_2H_3O_2$ is a weak acid. Its conjugate base, $C_2H_3O_2^-$, can act as a weak base in aqueous solutions.



$NH_3(aq)$ and $NH_4^+(aq)$: NH_3 is a weak base. Its conjugate acid, NH_4^+ , can act as a weak acid in aqueous solutions.

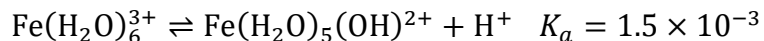


Soluble salts may contain ions that can affect the pH of an aqueous solution.

An anion that is the conjugate base of a weak acid can act as a weak base. For example, aqueous solutions of sodium acetate, $NaC_2H_3O_2$, are weakly basic due to $C_2H_3O_2^-$.

A cation that is the conjugate acid of a weak base can act as a weak acid. For example, aqueous solutions of ammonium chloride, NH_4Cl , are weakly acidic due to NH_4^+ .

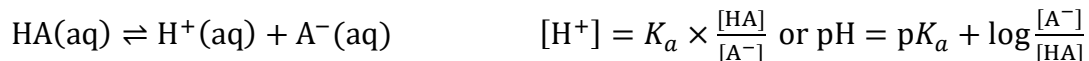
Certain hydrated metal ions show acidic behavior in water. While large metal cations with low charge density, such as Na^+ and K^+ , do not significantly affect the pH of a solution, some small, highly-charged hydrated metal ions do. An example is aqueous Fe^{3+} .



Experimental methods to determine equilibrium constants like K_a and K_b range from relatively straightforward to very complex, and the accuracy and precision of the results generated by these techniques can be quite variable. There are times when experimental ease is important and approximate values are completely acceptable. As a scientist, you will learn how to decide what your needs are and how best to meet them.

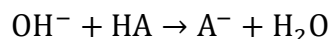
Buffered solutions (“buffers”) serve a critical function in many biological, environmental, experimental, and industrial processes by resisting large changes in solution pH upon the addition of small amounts of strong acid or strong base. Buffers typically contain a weak acid and its conjugate base (or a weak base and its conjugate acid).

Buffer pH primarily depends on the K_a of the weak acid component and the ratio of weak acid-conjugate base concentrations.



If the $\frac{[\text{A}^-]}{[\text{HA}]}$ ratio remains fairly constant, pH remains relatively stable.

A large pH increase is typically expected when even small amounts of OH^- are added to an aqueous solution. For example, adding 0.001 moles of OH^- to 1 L of water causes the pH to rise by 4 units from 7.0 to 11.0. In the case of a buffer, the added OH^- is neutralized by the weak acid component of the buffer, HA, generating the weaker conjugate base, A^- and water.



Although $[\text{HA}]$ decreases and $[\text{A}^-]$ increases, their ratio remains relatively constant, and the pH does not drastically change.

In part 1 of this experiment, you will calculate estimates of K_a and K_b values based on approximate pH values extracted from the colors of acid-base indicators in solution.

In part 2, you will investigate the effect of adding a small amount of the strong base NaOH on the pH of three solutions: 1) a weak acid; 2) a weak base; and 3) a buffer.

Equipment List

24-well well plate, pipets (part 1)

Deionized water, acid-base indicators, 0.10 M solutions (part 1)

pH meter, 100.00-mL volumetric flask, 1.00- and 5.00-mL volumetric pipets (part 2)

Calibration buffers, 1.0 M solutions (part 2)

Procedure

1. Obtain a 24-well well plate and wash it thoroughly.
2. There are eight liquids for which you will estimate pH. Complete one set, wash the well plate thoroughly, and then complete the second set.

There will be a flask of boiled deionized water available for you to use. Please do not set up your own.

Aside from water, the solutions are aqueous and 0.10 M.

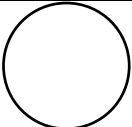
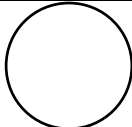
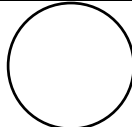
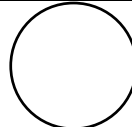
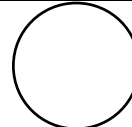
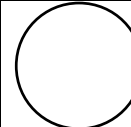
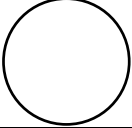
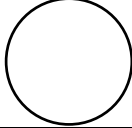
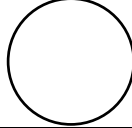
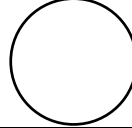
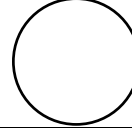
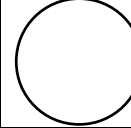
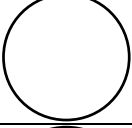
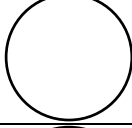
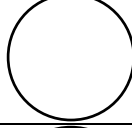
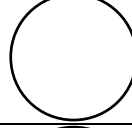
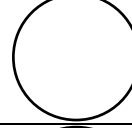
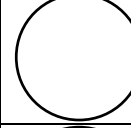
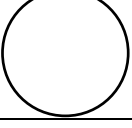
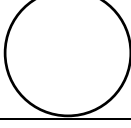
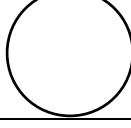
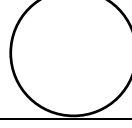
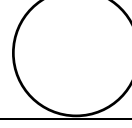
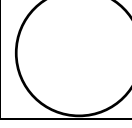
Set 1: deionized water, boiled deionized water, NaCl, NH₄Cl

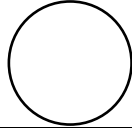
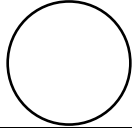
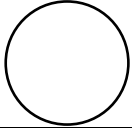
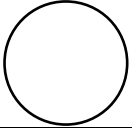
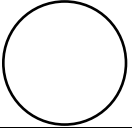
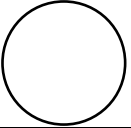
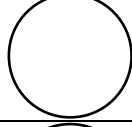
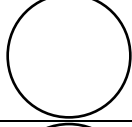
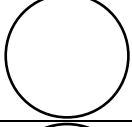
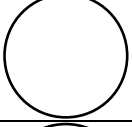
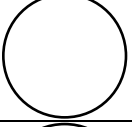
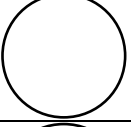
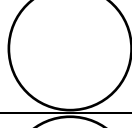
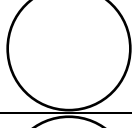
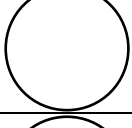
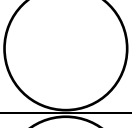
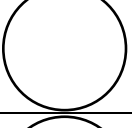
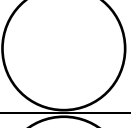
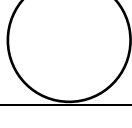
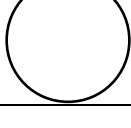
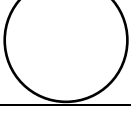
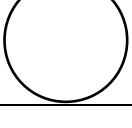
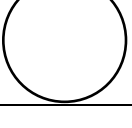
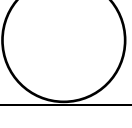
Set 2: NaC₂H₃O₂, ZnCl₂, KAl(SO₄)₂, Na₂CO₃

Weak Acid	Lit K_a at 25°C	Conjugate Base	Lit K_b at 25°C
NH ₄ ⁺	5.6×10^{-10}	NH ₃	1.8×10^{-5}
HC ₂ H ₃ O ₂	1.8×10^{-5}	C ₂ H ₃ O ₂ ⁻	5.6×10^{-10}
Zn(H ₂ O) ₆ ²⁺	1.0×10^{-9}	Zn(H ₂ O) ₅ (OH) ⁺	1.0×10^{-5}
Al(H ₂ O) ₆ ³⁺	1.0×10^{-5}	Al(H ₂ O) ₅ (OH) ²⁺	1.0×10^{-9}
HCO ₃ ⁻	5.6×10^{-11}	CO ₃ ²⁻	1.8×10^{-4}

Indicators: methyl orange, methyl red, bromothymol blue, phenol red, phenolphthalein, Alizarin yellow-R.

3. Use the dedicated pipet for each solution to fill each of the six wells across a row approximately 1/2-2/3 full.
4. Use the dedicated dropper to add one drop of indicator to each of the four wells down a column.

	Methyl orange	Methyl red	Bromo-thymol blue	Phenol red	Phenolphthalein	Alizarin yellow-R
deionized H ₂ O						
boiled deionized H ₂ O						
NaCl						
NaC ₂ H ₃ O ₂						

	Methyl orange	Methyl red	Bromo-thymol blue	Phenol red	Phenolphthalein	Alizarin yellow-R
NH ₄ Cl						
ZnCl ₂						
KAl(SO ₄) ₂						
Na ₂ CO ₃						

5. Place the well plate on a light background. Record the color of the solution in each well. Do one set, wash the well plate, and do the second set.

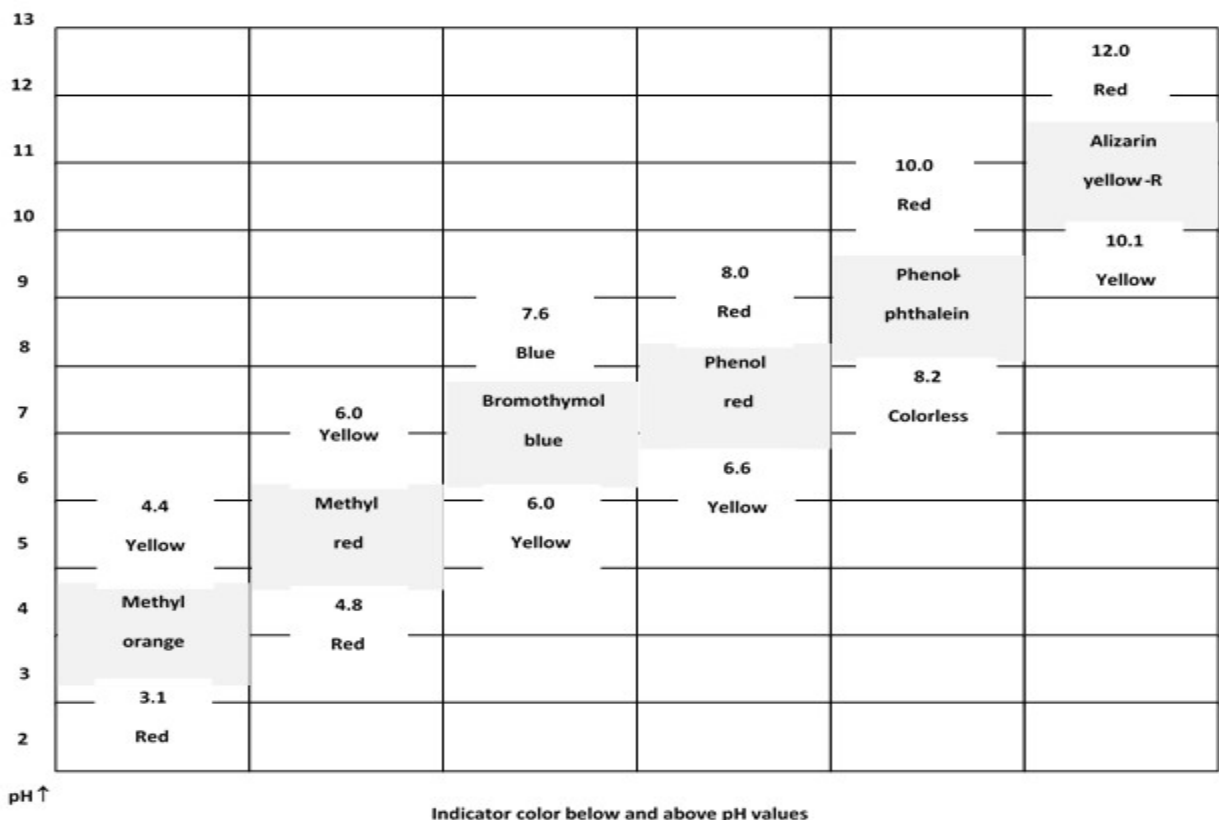
6. When finished, dispose of the solutions in the liquid waste container, wash the well plate very thoroughly, and return the well plate to the reagent bench. Finish the experiment before analyzing your data.

7. Think about the acid-base nature of any dissolved ions present in each of the liquid samples and predict the pH (or pH range) you expect to observe.

Set 1: *deionized water, boiled deionized water, NaCl, NH₄Cl*

Set 2: $\text{NaC}_2\text{H}_3\text{O}_2$, ZnCl_2 , $\text{KAl}(\text{SO}_4)_2$, Na_2CO_3

8. Estimate the pH of each of the eight solutions to one decimal place. Each solution has one pH value, not six. The indicator colors as a function of pH are shown.



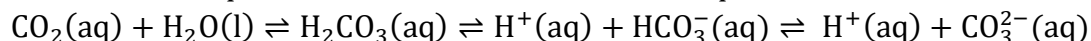
Look for “aboves”, “belows”, and “mixtures”. For example, consider the following observations regarding a solution’s color in each of the wells:

Indicator present	Color observed	pH assessment
Methyl orange	Yellow (“above”)	pH is greater than 4.4
Methyl red	Yellow (“above”)	pH is greater than 6.0
Bromothymol blue	Green (“mixture”)	pH is between 6.0 and 7.6
Phenol red	Orange (“mixture”)	pH is between 6.6 and 8.0
Phenolphthalein	Colorless (“below”)	pH is below 8.2
Alizarin yellow-R	Yellow (“below”)	pH is below 10.1

Final pH estimate: pH \approx 7.0

9. Compare your pH estimates to those expected for each liquid or solution. Do solutions of weak acids appear to have pH values less than 7.0? Weak bases, greater than 7.0?

What are possible reasons that the experimental results do not match what you expect?
How would the presence of dissolved CO₂ affect the pH of a solution?



10. Using your experimental pH values, calculate an estimate of the K_a for each weak acid and the K_b for each weak base to two significant figures. Assume one-to-one stoichiometry and less than 5% dissociation. Also assume that there are no other significant acidic or basic species present in each solution.

NH_4^+ , $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, $\text{Al}(\text{H}_2\text{O})_6^{3+}$:



$\text{C}_2\text{H}_3\text{O}_2^-$, CO_3^{2-} :



11. Calculate the percent error in each K_a or K_b . Why might the error be large? Think about how you determined the pH and how precise those values were. Also, consider your assumptions and the mathematical relationship between pH and H⁺ (pH is a logarithmic scale).

Part 2. The effect on pH by the addition of strong base – weak acid, weak base, and a buffer

Notes on using the pH meter

The pH probe should be kept in liquid. Do not let it sit out in air or to dry out.

Do not remove the probe from its holder (the “arm” on the pH meter).

Rinse the probe with deionized water between solutions to avoid contamination. Use your rinse bottle. Collect the rinse water in a labeled waste beaker.

When taking pH measurements, you must use the MANUAL MODE (see below).

All pH values should be recorded to two decimal places.

10. Calibrate the pH meter. Unless otherwise instructed, perform a three-point calibration using pH 4.00, 7.00, and 10.00 buffers.

Borrow one of the small cups of each buffer from the reagent bench. Rinse the probe, place it into the first buffer, and press CAL. The reading on the pH meter should stabilize on the pH of the buffer.

Repeat with the second and third buffers. Return the cups of buffer that you borrowed to the reagent counter. The probe should be placed into the storage solution until you are reading to make your pH readings.

Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, HAC

11. Borrow a small labeled beaker containing 1.0 M $\text{HC}_2\text{H}_3\text{O}_2$ from the reagent counter. Return the beaker to the reagent counter immediately after pipetting what you need.

12. Fill a labeled 100.00-mL volumetric flask approximately 1/4-full with deionized water.

13. Volumetrically pipet 5.00 mL of the 1.0 M $\text{HC}_2\text{H}_3\text{O}_2$ into the flask. Be very careful (see Caution).

Caution

Incorrect use of the pipet and pipetter can result in **serious injury**.

Please **do NOT force or jam the pipet** into the pipetter.

If you push too hard, the pipet can break and **cut your hand**.

Use **just enough force** to create a seal. The pipet does not “click” into place.

Hold both the pipet and pipetter at all times.

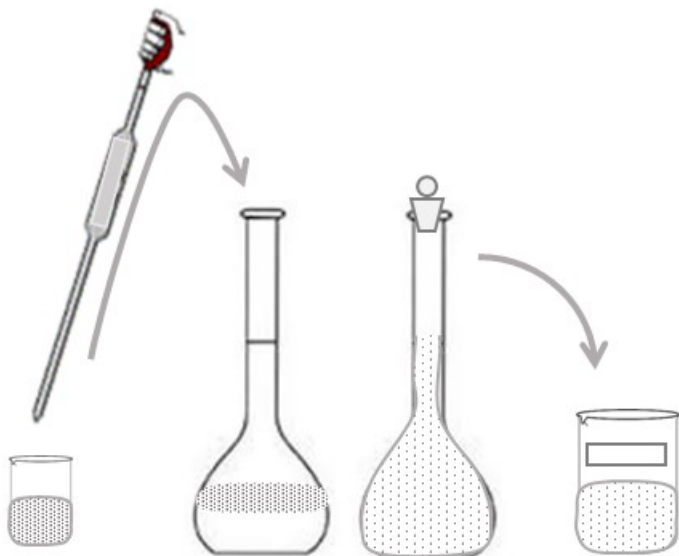
If you pull any solution into the pipetter, please give it to your TA so that it can be cleaned.

If you have trouble, **ask your TA for help**.

14. Fill the flask almost to the line on the neck of the volumetric flask with deionized water. Use a disposable pipet to adjust the level of the liquid so that the bottom of the meniscus is exactly on the line.

15. Insert the stopper into the flask, hold the stopper in firmly, and invert the flask to mix the solution thoroughly.

This method of preparing a solution via dilution is sometimes called the “sandwich” method – the more concentrated solution is “sandwiched” between two volumes of solvent.



16. Pour the resulting 0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ solution into a labeled beaker. Thoroughly wash the volumetric pipet and flask.

17. Record the pH of the 0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ solution to two decimal places. You must use the MANUAL mode.

Press READ on the pH meter. As the display on the pH meter blinks, count five seconds. Press READ again to freeze the pH value on the display. Record the pH to two decimal places.

18. Borrow a small labeled beaker containing 1.00 M NaOH from the reagent counter. Return the beaker to the reagent counter immediately after pipetting what you need.

19. Carefully volumetrically pipet 1.00 mL of the 1.00 M NaOH into the beaker of 0.0500 M $\text{HC}_2\text{H}_3\text{O}_2$. Stir with your glass stirring rod and record the new pH to two decimal places.

10. Dispose of the $\text{HC}_2\text{H}_3\text{O}_2$ solution in the liquid waste container. Wash all glassware thoroughly.

Sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, NaAc (acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$, Ac^-)

20. Repeat steps 2 – 10 using 5.00 mL of 1.0 M $\text{NaC}_2\text{H}_3\text{O}_2$ in place of the 5.00 mL of 1.0 M $\text{HC}_2\text{H}_3\text{O}_2$.

Acetic acid/acetate buffer, $\text{HC}_2\text{H}_3\text{O}_2/\text{C}_2\text{H}_3\text{O}_2^-$, HAc/ Ac^-

21. Repeat steps 2 – 10 using 5.00 mL of 1.0 M HC₂H₃O₂ and 5.00 mL of 1.0 M NaC₂H₃O₂ in place of the 5.00 mL of 1.0 M HC₂H₃O₂.

Follow your TA's instructions regarding cleanup. Dispose of all liquid waste in the liquid waste container. **Wash all glassware thoroughly.** Return anything borrowed clean. The used disposable pipet should be placed in the **broken glass container**, not the trash.

22. Calculate the expected pH before and after the addition of OH⁻ for each of the solutions (0.050 M HC₂H₃O₂, 0.050 M C₂H₃O₂⁻, and 0.050 M HC₂H₃O₂/0.050 M C₂H₃O₂⁻). Assume volumes are additive.

Use K_a , HC₂H₃O₂ = 1.8×10^{-5} and K_b , C₂H₃O₂⁻ = 5.6×10^{-10} . Keep extra significant figures, rounding the final pH to two decimal places. Refer to the following tables and equations to help you get started (note extra significant figures are carried for certain intermediate values).

Pre-OH⁻ pH:

Equilibrium	HC ₂ H ₃ O ₂	⇌	H ⁺	+	C ₂ H ₃ O ₂ ⁻
Initial	0.050		0		0
Change	-x		-x		+x
Equilibrium	0.050 - x		x		x

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \approx \frac{x^2}{0.050} \rightarrow [H^+] \approx x = \sqrt{(0.050)(1.8 \times 10^{-5})}$$

Post-OH⁻ pH:

Neutralization	HC ₂ H ₃ O ₂	+	OH ⁻	→	C ₂ H ₃ O ₂ ⁻	+	H ₂ O
Initial	0.050		0.010		0		----
Change	-0.010		-0.010		+0.010		
Equilibrium	0.040		0		0.010		

Equilibrium	HC ₂ H ₃ O ₂	⇌	H ⁺	+	C ₂ H ₃ O ₂ ⁻
Initial	0.0396		0		0.0099
Change	-x		-x		+x
Equilibrium	0.0396 - x		x		0.0099 + x

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \approx \frac{(x)(0.0099)}{0.0396} \rightarrow [H^+] \approx x = \frac{(0.0396)(1.8 \times 10^{-5})}{0.0099}$$

23. Compare your experimental pH values to those expected. What explanations can you give to account for any deviations?

Results / Sample Calculations

Complete the online inlab or write a lab report as directed by your TA.

pH and experimental K_a or K_b for part 1 liquids and solutions, % errors in K_a and K_b values
Experimental and theoretical pH before and after strong base addition for part 2 solutions

Discussion Questions and Review Topics

What did you do and what did you find?

Were your predictions for the pH of each liquid or solution in part 1 match what you observed (acidic, basic, or neutral)?

How did the K_a s and K_b s calculated using your pH estimates compare to literature values?

What are possible sources for the % errors? How could you improve the accuracy of the experiment?

Which solution in part 2 showed the smallest change in pH? The largest? Why?

What is different about the solution containing only $C_2H_3O_2^-$? When OH^- is added, is there an acid with which it can react?