

Acids, Bases, Salts, and Buffers

GOAL AND OVERVIEW

Hydrolysis of salts will be used to study the acid-base properties of dissolved ions in aqueous solutions. The approximate pH of these solutions will be determined using acid-base indicators. A buffer solution will be prepared, and its ability to moderate pH will be investigated alongside solutions that cannot function as buffers.

Objectives of the Data Analysis

- understand conjugate acid-base pairs and equilibria of weak acids and bases
- perform calculations involving ionic equilibria
- understand the components of buffer solutions and how they work to resist changes in pH

SUGGESTED REVIEW AND EXTERNAL READING

- data analysis review; relevant textbook information on acids, bases, salts, and buffers

BACKGROUND

Weak acids and bases in water

Brønsted-Lowry acids are proton donors and bases are proton acceptors. In water, an acid can donate a proton to water to form aqueous H^+ and the conjugate base; a base can accept a proton from water to form OH^- and the conjugate acid.

In acidic solutions, the concentration of $\text{H}^+(aq)$ is greater than the OH^- concentration and the pH is less than 7, while the reverse is true in basic solutions ($[\text{H}^+] < [\text{OH}^-]$, $\text{pH} > 7$). Aqueous solutions of substances such as HCl or $\text{HC}_2\text{H}_3\text{O}_2$ are expected to be acidic, while aqueous solutions of substances such as NaOH or NH_3 are expected to be basic.

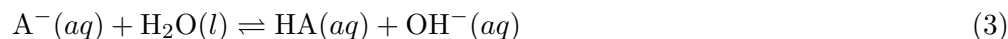
The dissolution of some salts into water can affect pH. For example, aqueous solutions of NaNO_2 and $\text{KC}_2\text{H}_3\text{O}_2$ are basic, whereas those of NH_4Cl and FeCl_3 are acidic. The dissolved ions have the potential to undergo *proton transfer reactions* with water to generate H^+ or OH^- . Anions that are the conjugate bases of weak acids react with water to form $\text{OH}^-(aq)$. Cations that are the conjugate acids of weak bases can undergo a proton transfer reaction with water to generate $\text{H}^+(aq)$.

Let HA represent a weak acid and A^- its conjugate base. A weak acid is one which does not completely dissociate in or react with a water solution. Instead, equilibrium is established. The equilibrium constant is called the acid dissociation constant, K_a .



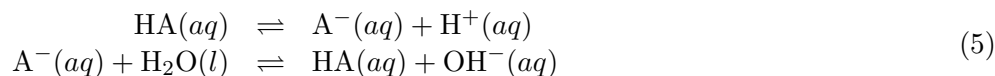
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (2)$$

A weak base is one which does not completely dissociate in or react with a water solution. Instead, equilibrium is established. The equilibrium constant is called the base dissociation constant, K_b .



$$K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} \quad (4)$$

Looking at the conjugate acid-base pair HA and A^- and their behavior in water:



the net ionic equation is:



and:

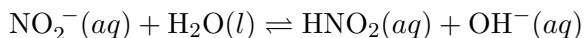
$$K_a K_b = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}^+][\text{OH}^-] = K_w. \quad (7)$$

K_w , water's auto-dissociation constant, is 1.0×10^{-14} at 25°C . If you know K_a for a weak acid, you can find K_b or vice versa (given K_b for a weak base, you can find K_a of the conjugate weak acid).

The stronger an acid, the larger its K_a and the weaker its conjugate base (smaller K_b). The weaker an acid, the smaller its K_a and the stronger its conjugate base (larger K_b). Similar statements apply to bases and their conjugate acids.

Here are several examples.

Weak base:

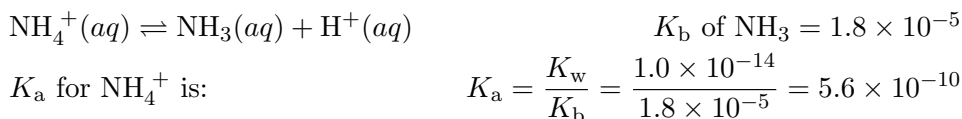


K_b for NO_2^- is:

$$K_a \text{ of } \text{HNO}_2 = 4.5 \times 10^{-4}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.2 \times 10^{-11}$$

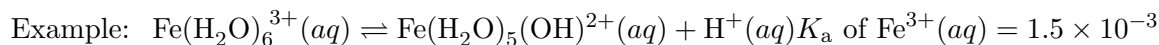
Weak acid:



Anions derived from strong acids, such as Cl^- , Br^- , I^- , HSO_4^- , ClO_4^- , and NO_3^- , do not react with water to affect pH. The parent acids are so strong in water that the conjugate bases are exceedingly weak.

Cations of the group 1A metals (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the group 2A metals (Ca^{2+} , Sr^{2+} , Ba^{2+}) do not react with water and are nonacids. They do not affect the pH of the solution.

Some highly-charged, rather small cations can produce an acidic solution. Examples would be hydrated Al^{3+} , Zn^{2+} , and Fe^{3+} ions. The hydrated ion can transfer a proton to water.



Anions with ionizable protons such as HCO_3^- , H_2PO_4^- , and HPO_4^{2-} are amphoteric – they may be acidic or basic, depending on the values of K_a and K_b for the ion. These types of species will not be considered in this lab.

The acidity, basicity, or neutrality of an aqueous salt solution can be predicted based on the strengths of the acid and base from which the salt was derived.

1 Cation from strong base; anion from strong acid

Ex. NaCl , KNO_3

Solution has $\text{pH} = 7$ (neutral)

2 Cation from weak base; anion from strong acid

Ex. NH_4Cl , $\text{Zn}(\text{NO}_3)_2$

Solution has $\text{pH} < 7$ (acidic) due to the hydrolysis of the cation

3 Cation from strong base; anion from weak acid

Ex. NaF , KNO_2

Solution has $\text{pH} > 7$ (basic) due to the hydrolysis of the anion

4 Cation from weak base; anion from weak acid

Ex. NH_4F , $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$

Solution pH is determined by the relative K_a and K_b of the cation and anion

In part 1 of this experiment, the pH of water and several salt solutions will be tested. Using the pH and initial concentration of each solution (and using the approximation that the extent of dissociation is small relative to that concentration), an approximate value of K_a or K_b can be calculated. A set of acid-base indicators will be used to estimate pH.

Buffers

A buffer solution resists large changes in pH upon the addition of small amounts of strong acid or strong base. A buffer has two components: one that will react with added H^+ and one that will react with added OH^- . Usually these two parts are a weak acid and its conjugate base (or vice versa). Buffers are often prepared by mixing a weak acid (or weak base) with a salt of that acid (or base). For example, a buffer could be made by adding $NaC_2H_3O_2$ solution to an $HC_2H_3O_2$ solution. Buffers of almost any pH can be made by proper choice of components and concentrations.

If significant concentrations of both a weak acid, HA, and its conjugate base, A^- , are present in the solution:

- added OH^- reacts with the weak acid: $HA + OH^- \rightleftharpoons H_2O + A^-$ $K_1 = 1/K_{b, A^-}$
- added H^+ reacts with the conjugate base: $A^- + H^+ \rightleftharpoons HA$ $K_2 = 1/K_{b, HA}$.

K_1 and K_2 are large, so the above reactions essentially go to completion. Once equilibrium is again reached, HA and A^- (and H_2O) are the dominant species in the solution.



The expression for $[H^+]$ indicates that the pH of the buffer depends on two factors:

- the value of K_a for the acid component of the buffer; and,
- the ratio of the weak acid to its conjugate base ($[HA]/[A^-]$).

Small amounts of added OH^- would slightly increase the A^- concentration. Small amounts of added H^+ would slightly increase the HA concentration. However, as long as the ratio of $[HA]/[A^-]$ is relatively constant, the pH change is small. Buffers work most effectively when $[HA]/[A^-]$ is roughly equal to 1 ($[HA] \approx [A^-]$).

When $[HA]$ equals $[A^-]$, $[H^+]$ equals K_a : $K_a = [H^+] \frac{[A^-]}{[HA]} = [H^+] \times 1 = [H^+]$ or $pH = pK_a$.

The Henderson-Hasselbach equation is often used to calculate approximate buffer pH.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (9)$$

Since the small amounts of acid or base that dissociate at equilibrium can usually be ignored, the initial concentrations of HA and A^- can be used directly in Eq. 7.

In part 2 of this experiment, you will prepare three solutions – one containing a weak acid; one containing the conjugate base; and, one containing both the acid and its conjugate base. You will measure the pH before and after a small amount of strong base is added and compare the relative ability of the three solutions to ‘buffer’ against pH change.

PROCEDURE

CAUTION: You are working with acids and bases. Handle them with caution and clean up spills.

Part 1: Salts and Solution pH (proton transfer reactions in water)

- 1 Boil approximately 250 mL deionized water and allow it to cool to room temperature. Use caution when heating/handling.
- 2 Determine the approximate pH of two water samples and six 0.1 M salt solutions by observing each solution's color in the presence of six different indicators.

The eight liquid samples to test are:

- unboiled deionized water
- boiled deionized water
- 0.1 M NaCl
- 0.1 M NH₄Cl
- 0.1 M NaC₂H₃O₂
- 0.1 M ZnCl₂
- 0.1 M KAl(SO₄)₂
- 0.1 M Na₂CO₃

The indicators to use are:

- methyl orange
- methyl red
- bromothymol blue
- phenol red
- phenolphthalein
- alizarin yellow-R

- 3 Use the schematics below as a guide. Rinse the well plate with a small amount of boiled deionized water and dry it before and after each set of observations.

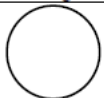
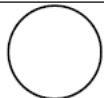
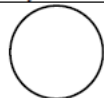
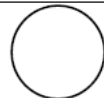
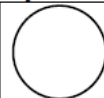
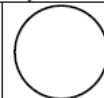
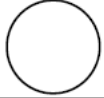
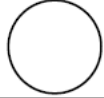
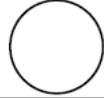
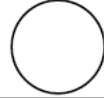
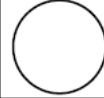
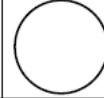
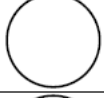
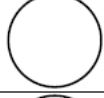
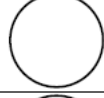
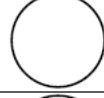
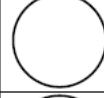
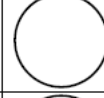
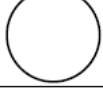
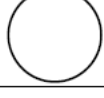
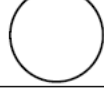
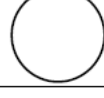
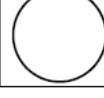
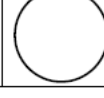
	Methyl orange	Methyl red	Bromo-thymol blue	Phenol red	Phenol-phthalein	Alizarin yellow-R
deionized H ₂ O						
boiled deionized H ₂ O						
NaCl						
NaC ₂ H ₃ O ₂						

Figure 1: Set 1

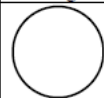
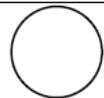
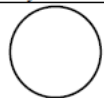
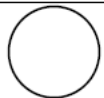
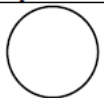
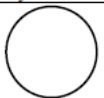
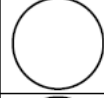
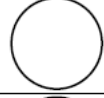
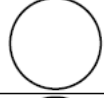
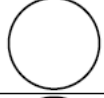
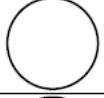
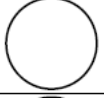
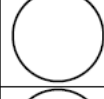
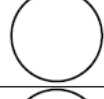
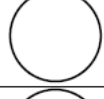
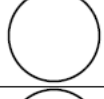
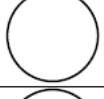
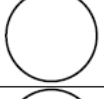
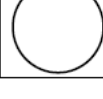
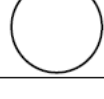
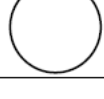
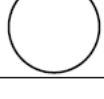
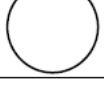
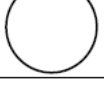
	Methyl orange	Methyl red	Bromo-thymol blue	Phenol red	Phenol-phthalein	Alizarin yellow-R
NH ₄ Cl						
ZnCl ₂						
KAl(SO ₄) ₂						
Na ₂ CO ₃						

Figure 2: Set 2

- Place 1 drop of an indicator into a well. Add a small volume (about 1 ‘squirt’ from the pipet) of the solution to be tested. Do not completely fill each well (about 1/2 way is enough). Test the solutions in two batches, four at a time.
- Record the color in each well for each solution.
- Wash the well plate thoroughly when finished and return it to the reagent bench.

Note – your TA may instruct you to split up the procedure for part 1 and share with another lab pair. Make sure you record all the required data for both sets of solutions.

Note – your TA may instruct you to start with part 2 and do part 1 after that. Please follow instructions.

Waste disposal: Dispose of your waste as instructed by your TA.

How to estimate the pH of — Na_2CO_3 as an example:

methyl orange appears yellow – pH is above 4.4

methyl red appears yellow – pH is above 6.0

bromothymol blue appears blue – pH is above 7.6

phenol red appears red – pH is above 8.0

phenolphthalein appears pink – pH is above 10.0

alizarin yellow-R appears orange – pH is in this range (~ 10.4)

— $\text{KAl}(\text{SO}_4)_2$ as an example:

methyl orange appears orange – pH is in this range (~ 3.8)

methyl red appears red – pH is below 4.8

no further data needed, but:

bromothymol blue appears yellow – pH is below 6.0

phenol red appears yellow – pH is below 6.6

phenolphthalein appears pink – pH is below 8.2

alizarin yellow-R appears orange – pH is below 10.1

Liquid or Solution	Experimental ~pH
unboiled H_2O (<i>dissolved CO_2</i>)	5.8
boiled H_2O (H_2O)	7.0
0.1 M NaCl (H_2O)	5.8
0.1 M $\text{C}_2\text{H}_3\text{O}_2^-$	8.1
0.1 M NH_4^+	4.4
0.1 M $\text{Zn}(\text{H}_2\text{O})_6^{2+}$	4.4
0.1 M $\text{Al}(\text{H}_2\text{O})_6^{3+}$	3.8
0.1 M CO_3^{2-}	10.4

Your solutions may look different, so make the best estimate you can for the approximate pH of each. Dissolved CO_2 can sometimes cause the solutions to test more acidic than expected.

- 8 The equilibrium expression(s) for the expected proton transfer reaction(s) in each solution are given below. Do your estimated pH values reflect the presence of excess H^+ or OH^- predicted by the reactions?

Liquid or Solution	Hydrolysis Equation
unboiled H ₂ O (dissolved CO ₂ ?)	$\begin{aligned} \text{H}_2\text{O}_{(l)} &\rightleftharpoons \text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \\ \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} &\rightleftharpoons \text{H}_2\text{CO}_{3(aq)} \rightleftharpoons \text{HCO}_3^-_{(aq)} + \text{H}^+_{(aq)} \end{aligned}$
boiled H ₂ O (H ₂ O)	$\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}^+_{(aq)} + \text{OH}^-_{(aq)}$
0.1 M NaCl (H ₂ O)	$\begin{aligned} \text{H}_2\text{O}_{(l)} &\rightleftharpoons \text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \\ \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} &\rightleftharpoons \text{H}_2\text{CO}_{3(aq)} \rightleftharpoons \text{HCO}_3^-_{(aq)} + \text{H}^+_{(aq)} \end{aligned}$
0.1 M C ₂ H ₃ O ₂ ⁻	$\text{C}_2\text{H}_3\text{O}_2^-_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2_{(aq)} + \text{OH}^-_{(aq)}$
0.1 M NH ₄ ⁺	$\text{NH}_4^+_{(aq)} \rightleftharpoons \text{NH}_3_{(aq)} + \text{H}^+_{(aq)}$
0.1 M Zn(H ₂ O) ₆ ²⁺	$\text{Zn}(\text{H}_2\text{O})_6^{2+}_{(aq)} \rightleftharpoons \text{Zn}(\text{H}_2\text{O})_5(\text{OH})^+_{(aq)} + \text{H}^+_{(aq)}$
0.1 M Al(H ₂ O) ₆ ³⁺	$\text{Al}(\text{H}_2\text{O})_6^{3+}_{(aq)} \rightleftharpoons \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}_{(aq)} + \text{H}^+_{(aq)}$
0.1 M CO ₃ ²⁻	$\text{CO}_3^{2-}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HCO}_3^-_{(aq)} + \text{OH}^-_{(aq)}$

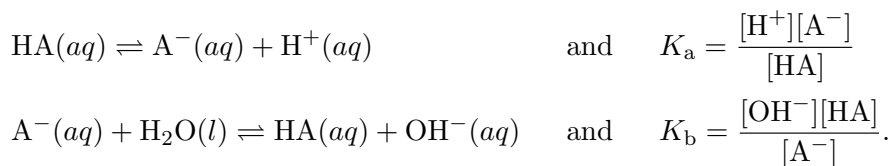
- 9 Using your pH values and the concentration of the solution, calculate the K_a or K_b for each cation or anion that hydrolyzes to two significant figures. Compare your calculated value to the literature value and give possible explanations for the deviation (if any).

Literature values:

Species	K_a at 25°C
HC ₂ H ₃ O ₂ , acetic acid	1.8×10^{-5}
Al(H ₂ O) ₆ ³⁺ , hydrated aluminum cation	1×10^{-5}
Zn(H ₂ O) ₆ ²⁺ , hydrated zinc cation	1×10^{-9}
H ₂ CO ₃ , carbonic acid	4.3×10^{-7}
HCO ₃ ⁻ , hydrogen carbonate ion	5.6×10^{-11}
NH ₄ ⁺ , ammonium ion	5.6×10^{-10}

If you need a K_b value, recall $K_b = K_w/K_a$

Recall:



Please assume the percent dissociation is small relative to the initial concentration of acid or base (0.1 M). In the weak acid solutions, recall $[\text{H}^+] = 10^{-\text{pH}}$, and please assume $[\text{H}^+] \approx [\text{A}^-]$ at equilibrium. In the weak base solutions, recall $[\text{OH}^-] = 1 \times 10^{-14}/[\text{H}^+]$, and please assume $[\text{OH}^-] \approx [\text{HA}]$ at equilibrium.

Example calculations:

Using pH = 10.4 for CO_3^{2-} solution: $\text{pOH} = 14 - 10.4 = 3.6$, so $[\text{OH}^-] = 2.5 \times 10^{-4}$.

CO_3^{2-}	+	H_2O	\rightleftharpoons	HCO_3^-	+	OH^-
0.10		---		0		0
-2.5×10^{-4}		---		$+2.5 \times 10^{-4}$		$+2.5 \times 10^{-4}$
~ 0.10		---		2.5×10^{-4}		2.5×10^{-4}

$$K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} \approx \frac{[2.5 \times 10^{-4}]^2}{[0.10]} = 6.3 \times 10^{-7}$$

Using pH = 3.8 for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ solution: $[\text{H}^+] = 1.6 \times 10^{-4}$.

$\text{Al}(\text{H}_2\text{O})_6^{3+}$	\rightleftharpoons	$\text{H}^+_{(\text{aq})}$	+	$\text{Al}(\text{H}_2\text{O})_5(\text{OH})_2^+$
0.10		0		0
-1.6×10^{-4}		$+1.6 \times 10^{-4}$		$+1.6 \times 10^{-4}$
~ 0.10		1.6×10^{-4}		1.6×10^{-4}

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \approx \frac{[1.6 \times 10^{-4}]^2}{[0.10]} = 2.6 \times 10^{-7}$$

The percent error relative to the literature values may be quite large. Think about how you determined the pH and how precise those values were. Also consider the impact of the log relationship between pH and $[\text{H}^+]$, as well as the assumptions you made.

Part 2a: pH of Buffer Solutions

- 1 Obtain about 10 mL 1 M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, "HAc") and about 10 mL 1 M sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$, "NaAc") solutions in small, labeled beakers.
- 2 Pipet 5 mL 1 M HAc into a labeled 100 mL volumetric flask and dilute to the mark with water.
- 3 Pipet 5 mL 1 M NaAc into a labeled 100 mL volumetric flask and dilute to the mark with water.
- 4 Pipet 5 mL 1 M HAc into a labeled 100 mL volumetric flask; pipet into the same flask 5 mL 1 M NaAc(aq). Dilute to the mark with water.
- 5 The above steps should provide you with 100 mL of each of the following: acetic acid solution (HAc), acetate (NaAc) solution, and acetic acid/acetate solution (HAc/Ac⁻). Calculate the initial molarity of HAc, Ac⁻, and HAc, Ac⁻ in each solution.
- 6 Measure the pH of the solutions using a calibrated pH meter (see instructions in lab). The pH meters are delicate and you need to read the printed instructions carefully (and follow the TA's instructions, too). Record each pH value to two decimal places.
- 7 Save the solutions for part 2b.

- 8 Calculate the expected pH of the 0.05 M HAc, 0.05 M Ac⁻, and 0.05 M HAc/0.05 M Ac⁻. Your pH values should be ~3.02, 8.72, and 4.74, respectively. Compare your measured value to the theoretical value and give possible explanations for the deviation (if any).

ICE table to help you get started:

HAc _(aq)	⇌	H ⁺ _(aq)	+	Ac ⁻ _(aq)
0.05		~0		0.00
-x		+x		+x
~0.05		x		x

Ac ⁻ _(aq)	+	H ₂ O	⇌	OH ⁻ _(aq)	+	HAc _(aq)
0.05		---		~0		0.00
-x		---		+x		+x
~0.05		---		x		x

HAc _(aq)	⇌	H ⁺ _(aq)	+	Ac ⁻ _(aq)
0.05		~0		0.05
-x		+x		+x
~0.05		x		~0.05

Part 2b: Effect of Acid and Base on Buffer pH

- 9 Pipet 1 mL 1.0 M NaOH into the HAc solution and record the pH.

Note – there is a weak acid present to react with the added OH⁻. Do you expect a huge jump in pH here?

- 10 Pipet 1 mL 1.0 M NaOH into the Ac⁻ solution and record the pH.

Note – there is only a weak base present in the initial solution, so what do you think added OH⁻ will do to the pH here?

- 11 Pipet 1 mL 1.0 M NaOH into the HAc/Ac⁻ and record the pH.

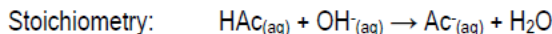
Note – the original solution is a buffer, so do you expect the pH change to be relatively large or small here?

- 12 Please clean the pH meter and leave the electrode immersed in the pH = 7 buffer (yellow solution).

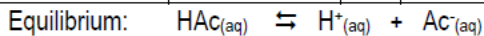
Waste disposal: Follow your TA's instructions.
Clean all equipment and return it to the correct location.

- 13 Calculate the expected pH of 0.05 M HAc, 0.05 M Ac⁻, and 0.05 M HAc/0.05 M Ac⁻ after the addition of 1 mL 1.0 M NaOH to each. Your values should be ~4.14, 12.00, and 4.92, respectively. Compare your measured pH value to the theoretical value and give possible explanations for the deviation (if any).

Tables to help you get started:

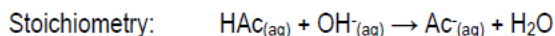


	HAc	+	OH ⁻	⇌	Ac ⁻	+	H ₂ O
Before rxn	0.005mol		0.001		0.000		---
Change	-0.001		-0.001		+0.001		---
After rxn	~0.004		~0		0.001		---

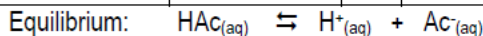


HAc _(aq)	⇌	H ⁺ _(aq)	+	Ac ⁻ _(aq)
0.04		~0		0.01
-x		+x		+x
~0.04		x		~0.01

Stoichiometry: $\text{Ac}^{-}(aq) + \text{OH}^{-}(aq) \rightarrow \text{Ac}^{-}(aq) + \text{OH}^{-}(aq)$; think about $[\text{OH}^{-}]$ from NaOH vs. Ac^{-}



	HAc	+	OH ⁻	⇌	Ac ⁻	+	H ₂ O
Before rxn	0.005mol		0.001		0.005		---
Change	-0.001		-0.001		+0.001		---
After rxn	~0.004		~0		0.006		---



HAc _(aq)	⇌	H ⁺ _(aq)	+	Ac ⁻ _(aq)
0.04		~0		0.06
-x		+x		+x
~0.04		x		~0.06

REPORTING RESULTS

Complete your lab summary or write a report (as instructed).

Abstract

Results

Part 1. Hydrolysis equation for each solution; K_a or K_b of each liquid or solution; percent error

Part 2a. Measured and expected pH of solutions before OH^{-} addition

Part 2b. Measured and expected pH of solutions after OH^{-} addition

Sample Calculations

Part 1. K_a or K_b of each hydrolyzed species; percent error

Part 2a. Expected pH of solutions before OH^{-} addition

Part 2b. Expected pH of solutions after OH^{-} addition

Discussion/Conclusions

Part 1. Did the pH of the solutions match what might be predicted based on the cation and anion provided by the salt? How good were your measured K_a or K_b values?

Part 2a. Did the measured pH match the expected pH?

Part 2b. Did the measured pH match the expected pH? Which solution showed the greatest change in pH? Which showed the least? Why?

Review Questions