# **EXPERIMENT 3** Determining K<sub>a</sub>

# Introduction

In the previous lab, acid and base solutions were evaluated to determine their general levels of acidity using pH. In this experiment, the pH of a solution will be used to determine the degree of dissociation of the hydrogen ion from the original acid. To briefly review the **Bronsted-Lowry theory**, an acid is defined a compound that donates a hydrogen ion and a base accepts a hydrogen ion. When an acid is added to water, the liquid water acts as a base according to the following chemical reaction:

$$HCI\text{+}H_2O \rightarrow H_3O^{+}\text{+}CI^{-}$$

In this example, the HCl dissociates completely and donates a hydrogen ion,  $H^+$ , to a water molecule which acts as a base by receiving the  $H^+$ . The resulting product is a hydronium ion,  $H_3O^+$ , that changes the pH of the water and a Cl<sup>-</sup> that acts as a spectator ion. There is 100% dissociation of the HCl, so the concentration of the original HCl solution is the same as the concentration of the hydronium ion.

Strong acids and bases are acidic or basic compounds that completely dissociate as in the equation above. As a result, the concentration of the hydronium ion can be calculated directly from the initial concentration of the HCl. For example, in water 1M HCl would produce  $1M H_3O^+(aq)$  and  $1M Cl^-(aq)$ . There would be no HCl left in solution at the end of the reaction. All of the reactant has been used up to form product. The pH of the solution can then be directly calculated from the initial concentration of the strong acid and base using the equation;  $pH = -log(H_3O^+)$ .

However, the determination of pH in a weak acid or base solution is much more complicated. In these solutions, the pH is a function of both the initial concentration of the weak acid or base and the degree of dissociation of the H<sup>+</sup>. To determine the degree of dissociation of the acid, HA, we need to know the equilibrium constant that governs the ratio between the reactants and products in the weak acid equilibrium. When the equilibrium involves a weak acid, we refer to the equilibrium constant as an "<u>acid dissociation constant</u>" and give it the symbol,  $K_a$ .

$$HA + H_2O \leftrightarrow H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

#### The Acid Dissociation Constant, Ka

Acid dissociation constants have been determined for many different weak acids at approximately room temperature. Tables of these dissociation constants permit a researcher to determine the pH of a solution without performing experiments and to calculate the concentration of a weak acid needed to produce the desired pH of a final solution. You used a given  $K_a$  in the last experiment to do your pH calculations, but the  $K_a$  for each acid had to be determined experimentally before being tabulated. You will repeat the procedures used to determine the Ka for an unknown acid in a similar manner to the researchers who first developed the  $K_a$  tables.

In the previous experiment, you used an ICE table to determine the pH of a solution using the tabulated  $K_a$ . In this lab, the pH of a known acid solution will be used to determine equilibrium concentration of the  $H_3O^+$  using the following equation.

pH = 
$$-\log[H_3O^+]$$
 and with a quick rearrangement,  $[H_3O^+] = 10^{-pH}$ 

Once you know the concentration of the  $H_3O^+$ , you can use an ICE table to determine the concentrations of the A- and the HA. Once you have all 3 of these values, you can then determine the K<sub>a</sub> of the acid.

#### Using an ICE Table for Weak Acid Equilibria

The ICE table set up for a weak acid equilibrium follows the same format as in the previous lab. First, you write the balanced chemical reaction and record the initial concentrations of your reactants and products. Then you use the balanced equation to determine the changes that will take place based on the stoichiometry. Reactants will always decrease in concentration, so you use a negative coefficient before the variable, x. Products increase, so use a positive value of x. The value of the coefficient in front of the x is the value of the coefficient in the chemical equation.

Finally, add the values or formulas on the initial and change lines together to find the final formula for the equilibrium concentrations. Note that water is not used at all in the equilibrium as it is a pure liquid and pure liquids and solids cannot change their concentrations and thus will not affect the equilibrium. For the example below, we start with a 2.0M solution of HA in water.

	HA(aq)	+	H <sub>2</sub> O (I)	与	H₃O⁺ (aq) +	A⁻(aq)
Initial	2.0				0	0
Change	-1x				+1x	+1x
Equilibrium	(2.0-1x)				(0+1x)	(0+1x)

If you know the pH of the solution, then solve for the  $H_3O^+$  (aq) and solve for  $K_a$  using the equilibrium constant expression shown below.

$$K_{a} = \frac{[H_{3}O^{+}][A^{-}]}{[HA]} = \frac{[x][x]}{[2.0 - x]}$$

#### Relationship between pH, H<sub>3</sub>O<sup>+</sup> and the Initial Acid Concentration

K<sub>a</sub> is constant for a particular weak acid at a particular temperature and is independent of the initial acid concentration. Therefore, if you vary the initial concentration of the acid, [HA], the pH will change to compensate and maintain the equilibrium between the reactants and products.

$$HA(aq) + H_2O(I) \implies H_3O^+(aq) + A^-(aq)$$

For example, if you increase the concentration of HA, you will get more  $H_3O^+$  produced in the solution. An increase in  $H_3O^+$  means the solution is more acidic and a lower pH will be recorded. A lower pH would be expected because logically, if you add more acid to water, the solution should become more acidic.

#### In Your Lab....

For your experiment, you will measure the pH of several different concentrations of the same acid and calculate the  $K_a$  for each to demonstrate that  $K_a$  is independent of the solution concentration. You will prepare these solutions by starting with a stock acid solution and use NaOH, a strong base to react with some of the acid according to the following equation.

NaOH+ HA  $\rightarrow$  H<sub>2</sub>O + Na<sup>+</sup> + A<sup>-</sup>

If you add NaOH to the solution in the previous example, you end up changing the initial concentrations of both the HA and A-. This is because for every mole of NaOH you add; you remove 1 mole of HA, thus decreasing the initial concentration of HA. A- is formed as a result of this reaction and thus increases the initial amount of A- in the ICE table. The additional Na<sup>+</sup> that is added to the solution does not affect the pH of the solution.

	HA(aq) + H <sub>2</sub> O (I)	⇆	H₃O⁺ (aq) +	A⁻(aq)
Initial	(2.0-1.0M = 1.0M)		0M	1.0M
Change	-1x		+1x	+1x
Equilibrium	(1.0-1x)		(0+1x)	(1.0+1x)

After preparing the solutions, you will record the pH and calculate the  $H_3O^+$  in each one. Then you will use an ICE table to determine the equilibrium concentrations of the A- and HA. Once you have established the concentrations of all of the reactants and products at equilibrium, you can calculate  $K_a$  for the acid.

Once you have determined the  $K_a$  for the acid, you will compare it to a list of common weak acids (Table 1) to determine the identity of the weak acid based on its calculated  $K_a$ .

Table 1		
Substance	Formula (HA)	K <sub>a</sub> at 25°C
lodic acid	HIO <sub>3</sub>	2.0×10 <sup>-1</sup>
Chlorous acid	HCIO <sub>2</sub>	1.0×10 <sup>-2</sup>
Nitrous acid	HNO <sub>2</sub>	1.0×10 <sup>-3</sup>
Formic acid	HCHO <sub>2</sub>	2.0×10 <sup>-4</sup>
Acetic acid	$HC_2H_3O_2$	2.0×10 <sup>-5</sup>
Hypochlorous acid	HOCI	5.0×10 <sup>-8</sup>
Hypobromous acid	HOBr	2.0×10 <sup>-9</sup>
Hydrocyanic acid	HCN	5.0×10 <sup>-10</sup>
Hypoiodous acid	HOI	2.0×10 <sup>-11</sup>

# Chemical Hazards

## 1.0M Weak Acid Solution

NFPA RATING: HEALTH: 1 FLAMMABILITY: 0 REACTIVITY: 0

INHALATION:
Move person into fresh air immediately. Contact TA immediately.
DERMAL EXPOSURE:
Wash off with soap and plenty of water.
EYE EXPOSURE:
Flush with copious amounts of water for at least 15 minutes. Assure adequate flushing by separating the eyelids with fingers. Contact your TA immediately.

## pH 7 Buffer Solution

NFPA RATING: HEALTH: 0 FLAMMABILITY: 0 REACTIVITY: 0

## DERMAL EXPOSURE:

Wash off with soap and plenty of water. **EYE EXPOSURE:** Flush with copious amounts of water. Assure adequate flushing by separating the eyelids with fingers. Contact your TA immediately.

## 0.50M Sodium Hydroxide Solution

NFPA RATING: HEALTH: 1 FLAMMABILITY: 0 REACTIVITY: 1

#### ORAL EXPOSURE

Caustic. If swallowed, wash out mouth with water provided person is conscious. Do not induce vomiting. Contact your TA immediately.

#### DERMAL EXPOSURE

Caustic. In case of extensive skin contact, flush with copious amounts of water for at least 15 minutes. Remove contaminated clothing and shoes. Contact your TA immediately.

#### EYE EXPOSURE

Caustic. In case of contact with eyes, flush with copious amounts of water for at least 15 minutes. Assure adequate flushing by separating the eyelids with fingers. Contact your TA immediately.

# **Experiment 3: Prelab Worksheet**

(Submit through Brightspace before coming to lab)

Name: \_\_\_\_\_ Date: \_\_\_\_\_ Section: \_\_\_\_\_ Grade: \_\_\_\_\_

Record all values with the correct number of significant figures and units.

Place all answers on the line next to the question.

Show calculations for any numerical answers.

See any 114 TA in the help office before your prelab is due if you have any questions.

Your answer must be completely correct to get any credit for the answer, no partial credit.

# You make a solution of a weak acid with a pH of 3.75 and the $pK_a$ is 5.42

- 1. Is the solution acidic or basic?
- 2. Calculate the  $[H_3O^+]$ .
- 3. Calculate the pOH
- 4. Calculate the [OH<sup>-</sup>]

- 5. Calculate the pK<sub>b</sub>
- 6. Calculate the K<sub>b</sub>.

For a solution of an aqueous hypochlorous acid solution, the  $K_a$  is 5.0 x 10<sup>-8</sup> and [HOCI] is 0.050M.

7. Calculate the pH of this solution.

8. You add 2.0mL of 1.0M NaOH to the 1.0L acid solution, what is the new concentration of [HOCI]?

You make 50.00mL of a 0.045M solution of NaOH from a 2.5M stock solution.

9. How many milliliters of the concentrated stock solution will you need?

10. What is the pH of the diluted solution?

# **Experiment 3: Experimental Procedures and Data Sheet**

Submit as part of your informal report

Na	ame:	Date:	Section:
ΤA	A Signature:		
Re	I data must be written in pen at the time it is collected. <b>Pen</b> ecord all measurements with the correct number of significa A signature and TA initials on any changes made to the dat	ant figures and units.	your data is invalid
1.	Record the exact concentrations of the sodium hydroxide	and the weak acid s	olutions.
	NaOH Concentration: We	ak Acid Concentratior	n:
~			

- Use your 10.0mL graduated cylinder to transfer exactly 8.00 mL of acid to a clean dry 25 mL volumetric flask.
- 3. Use your 10.0mL graduated cylinder to transfer exactly 2.50 mL of NaOH to the flask containing the 8.00 mL of acid. Fill the 25 mL volumetric to the line with distilled water and swirl to mix.
- 4. Pour the mixed solution into a scintillation vial. Label the vial "Solution 1".
- 5. Repeat this procedure for the remaining 3 solutions given in the table below.

Solution	Volume of 1.00M weak acid	Volume of 0.50M NaOH
number	mL	mL
1	8.00	2.50
2	8.00	5.00
3	8.00	7.50
4	8.00	10.00

- 6. Calibrate your pH meter with the pH 7 buffer. (See experiment 4 lab procedures if necessary)
- 7. Once calibrated, rinse off the bulb of the pH meter with distilled water and then insert the pH meter into Solution 1.
- 8. Gently stir the solution with the pH meter and watch the reading. When the reading has stabilized on the pH meter, record the pH value on your data sheet. Repeat for the other 3 solutions.

Solution 1 pH:	Solution 3 pH:	
Solution 2 pH:	Solution 4 pH:	

#### <u>Cleanup</u>

- 1. Rinse the pH meter with distilled water and return it to the buffer solution.
- 2. Empty your solution into the waste container and rinse your volumetric flask out well with distilled water.
- 3. Dispose of solutions in the waste container provided.
- 4. Rinse all glassware with distilled water and remove markings with acetone if necessary.

#### **Calculations**

Do all calculations in the **Calculations** section and complete the results table before leaving lab. Use more paper if necessary. These calculations MUST be done **IN THE LAB** and checked by your TA before leaving. You will be expected to do these calculations WITHOUT the instructions during next week's Concept Review.

# Grading

<u>Points</u>			
	Neatness and Clarity of Data	5pts	 _pts
	Significant figures and units	5pts	 _pts
	All data is present	10pts	 _pts
Deduc	tions (sliding based on TA discretion)		
	Lab area left unclean	20pts	 _pts
	Improper waste disposal	20pts	 _pts
	Disruptive behavior	20pts	 _pts
	Other:		 _pts
Plagia	arism!!! Data are identical to anoth	er student 100pts	 _pts

# **Grade for Experimental Procedures and Data**

# **Experiment 3: Results Table**

Submit as part of your informal report

Name:	 Date:	Section:
TA Signature:	 (after calculations	are done during lab)

Record all results with the correct number of significant figures and units

K <sub>a</sub> Calculations	Solution 1	Solution 2	Solution 3	Solution 4
[H <sub>3</sub> O <sup>+</sup> ]				
M <sub>dil. acid</sub>				
M <sub>dil. NaOH</sub>				
НА				
A-				
H₃O⁺				
НА				
A-				
Ka				
Average K <sub>a</sub>				
Identity of acid				
Accepted K <sub>a</sub> of acid				

# Grading

<u>Points</u>		
Significant figures and units	5pts	pts
Table is neat and legible	5pts	pts
All results are present	10pts	pts
Deductions (sliding based on TA dis	scretion)	
Results do not make sense	20pts	pts
Results do not match data	20pts	pts
Other:		pts
Plagiarism!!! Results are identication	al to another student 100pts	pts

Grade on results table

\_\_\_\_pts

# **Experiment 3: Calculations**

Submit as part of your informal report

You must do these calculations out with your TA before you leave the lab.

# Concentration of $[H_3O^+]$ for the ICE Table, x

Use the pH value that you recorded from your data to find the hydronium ion concentration of the solution using the equation below. Repeat for all of your solutions.

 $x = [H_3O^+] = 10^{-pH}$ 

Solution 1:	 Solution 3:	
Solution 2:	 Solution 4:	

# Concentration of Diluted Weak Acid before the Addition of NaOH, Mdil. acid

Multiply the concentration of the weak acid recorded on the bottle in the hood by the number of milliliters of acid dispensed into the volumetric flask. Divide this number by 25.00mL, the total volume of the dilute acid.

$$M_{\rm dil.acid} = \frac{M_{\rm conc.acid} V_{\rm conc.acid}}{V_{\rm dil.acid}}^{\dagger}$$

Solution 1: \_\_\_\_\_\_ Solution 3: \_\_\_\_\_\_

## Concentration of Diluted NaOH, Mdil. NaOH

Solution 2:

Multiply the concentration of the sodium hydroxide, NaOH, recorded on the bottle in the hood by the number of milliliters of NaOH dispensed into the volumetric flask. Divide this number by 25.00mL, the total volume of the dilute NaOH.

\* \*

Solution 4:

$$M_{dil.NaOH} = \frac{M_{conc.NaOH}}{V_{NaOH}}$$
Solution 1: \_\_\_\_\_\_ Solution 3: \_\_\_\_\_\_
Solution 2: \_\_\_\_\_\_ Solution 4: \_\_\_\_\_\_

. .

# Concentration of Diluted Weak Acid After the Addition of NaOH, HA

Each mole of NaOH added to the acid solution uses up 1 mole of the acid. To calculate the concentration of the weak acid to be used in the ICE table, subtract the concentration of the diluted NaOH from the concentration of the diluted weak acid.

	1NaOH+ 1HA $\rightarrow$ 1H <sub>2</sub> O + 1Na <sup>+</sup> + 1A <sup>-</sup>	
	M acid in ICE table = M dil. Acid – M dil. NaOH	
Solution 1:	Solution 3:	
Solution 2:	Solution 4:	

## Concentration of Weak Base, A<sup>-</sup>

ince each mole of NaOH removes the H<sup>+</sup> from an acid molecule, HA, the number of moles of A- produced will equal the moles of NaOH added. Therefore, the molarity of the A- will be equal to the molarity of the diluted NaOH. Use this in the ICE table for the initial value of A<sup>-</sup>(aq).

Solution 1:	 Solution 3:	

 Solution 2:
 Solution 4:

### Equilibrium Concentrations, H<sub>3</sub>O<sup>+</sup>, HA, and A<sup>-</sup>

Use an ICE table for each concentration of the weak acid and NaOH. Use the values calculated in the previous sections. You will need 1 ICE table for each set of acid/NaOH concentrations.

	HA(aq)	+	H <sub>2</sub> O (I)	⇆	H₃O⁺ (aq) +	A⁻(aq)
Initial	HA				0M	A⁻
<b>C</b> hange	Х				Х	х
Equilibrium	HA -x				х	A⁻ + x

 $H_3O^+$  is the concentration of  $H_3O^+$  found from the pH and is equal to x. HA is the HA concentration initially calculated for the ICE table minus the  $H_3O^+$  concentration. A<sup>-</sup> is the A<sup>-</sup> concentration initially calculated for the ICE table plus the  $H_3O^+$  concentration.

Find 1 set of each of these values for each pair of weak acid/NaOH concentrations.

Note:  $H_3O^+$  is often negligible compared to HA, so HA at equilibrium is often equal to the initial concentration of HA. Don't be surprised if this happens. Use the rules for significant figures to decide if x is negligible relative to an initial concentration. The same rules apply to A<sup>-</sup> in the ICE table as well.

Solution 1: H <sub>3</sub> O <sup>+</sup>	HA	A <sup>-</sup>
Solution 2: H <sub>3</sub> O <sup>+</sup>	НА	A <sup>-</sup>
Solution 3: H <sub>3</sub> O <sup>+</sup>	HA	A <sup>-</sup>
Solution 4: H <sub>3</sub> O <sup>+</sup>	HA	A

#### Calculation of K<sub>a</sub>

Use the values found for the ICE table variables in the equilibrium constant expression, Ka. Repeat for each ICE table.

$$K_{a} = \frac{[H_{3}O^{+}][A^{-} + x]}{[HA - x]}$$

 Solution 1:
 \_\_\_\_\_\_
 Solution 3:
 \_\_\_\_\_\_

 Solution 2:
 Solution 4:

## Identification of the Weak Acid

Find the average value for the  $K_a$  of the weak acid from the  $K_a$  values determined from each ICE table. Compare them to the values given in Table 1 and record the identity of the weak acid.

Average K<sub>a</sub>

Identity of weak acid