

# EXPERIMENT 5

## Determining $K_a$

### Introduction

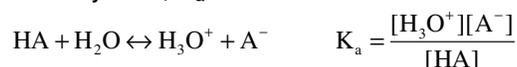
In the previous lab, compounds were evaluated as to their general levels of acidity. In this experiment, the specific pH of a compound will be determined based on the specific degree of dissociation of the hydrogen ion from the acid resulting in a numerical value for the pH. To briefly review the Bronsted-Lowry 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:



In this example, the HCl dissociates completely and donates a hydrogen ion,  $\text{H}^+$ , to a water molecule which acts as a base by receiving the  $\text{H}^+$ . The resulting product is a hydronium ion,  $\text{H}_3\text{O}^+$ , that changes the pH of the water and a  $\text{Cl}^-$  that acts as a spectator 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  $\text{H}_3\text{O}^+(\text{aq})$  and 1M  $\text{Cl}^-(\text{aq})$ . 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;  $\text{pH} = -\log(\text{H}_3\text{O}^+)$ .

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  $\text{H}^+$ . 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 "acid dissociation constant" and give it the symbol,  $K_a$ .



### The Acid Dissociation Constant, $K_a$

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. However, the  $K_a$  for each acid had to be determined experimentally before being tabulated. You will repeat the procedures used to determine the  $K_a$  for an unknown acid in a similar manner to the researchers who first developed the  $K_a$  tables.

In the previous experiment, you used a spectrophotometer to identify the concentration of the product of your equilibrium. From this you used an ICE table to determine the equilibrium concentrations of the reactants. In this lab, the pH of a known acid solution will be used to determine equilibrium concentration of the  $\text{H}_3\text{O}^+$  using the following equation.

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \text{ and with a quick rearrangement, } [\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

Once you know the concentration of the  $\text{H}_3\text{O}^+$ , you can use an ICE table to determine the concentrations of the  $\text{A}^-$  and the HA. Once you have all 3 of these values, you can then determine the  $K_a$  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 any other equilibrium reaction. 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 (l)	↔	H <sub>3</sub> O <sup>+</sup> (aq)	+	A <sup>-</sup> (aq)
Initial	2.0M				0M		0M
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<sub>3</sub>O<sup>+</sup> (aq) and solve for K<sub>a</sub> using the equilibrium constant expression shown below.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[x][x]}{[2.0 - x]}$$

### 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.



For example, if you increase the concentration of HA, you will get more H<sub>3</sub>O<sup>+</sup> produced in the solution. An increase in H<sub>3</sub>O<sup>+</sup> 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<sub>a</sub> for each to demonstrate that K<sub>a</sub> 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.



If you add NaOH to the solution in the example given previously until you reach a concentration of 1.0M, you end up changing the initial concentrations of both the HA and A<sup>-</sup>. This is because for every mole of NaOH you add; you remove 1 mole of HA, thus decreasing the initial concentration of HA. A<sup>-</sup> is formed as a result of this reaction and thus increases the initial amount of A<sup>-</sup> 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 (l)	↔	H <sub>3</sub> O <sup>+</sup> (aq)	+	A <sup>-</sup> (aq)
Initial	(2.0-1.0M = 1.0M)				0M		1.0M
Change	-1x				+1x		+1x
Equilibrium	(1.0-1x)				(0+1x)		(1.0+1x)

Once the solutions have been prepared, you will record the pH of each one and calculate the H<sub>3</sub>O<sup>+</sup> in each. You will then use an ICE table to determine the equilibrium concentrations of the A<sup>-</sup> and HA. Once you have established the concentrations of all of the reactants and products at equilibrium, you can calculate K<sub>a</sub> for the acid.

Once you have determined the K<sub>a</sub> for the acid, you will compare it to a list of common weak acids to determine the identity of the weak acid based on its calculated K<sub>a</sub>.

## Laboratory Equipment Procedures

### ***Using the MeasureNet System for pH Measurements***

The pH meter should already be connected to the MeasureNet system at the start of lab. Follow the instructions below to set up for pH measurements.

#### **Setting up system for pH measurements**

1. Press the On/Off button to turn on power to the MeasureNet station.
2. Press Main Menu.
3. Press F3- pH/mV.
4. Press F1- pH v TIME.
5. Press DISPLAY.
6. If your display does not read between 6.95 and 7.05, follow the instructions below to calibrate the electrode.

#### **Electrode Calibration**

1. Remove cap and pH electrode from the storage bottle.
2. Insert the pH electrode into the storage bottle and screw on the lid.
3. Press CALIBRATE on the MeasureNet station.
4. Ask the TA for room temperature and enter the temperature into the MeasureNet station.
5. Press ENTER.
6. Enter 7 for the pH of the buffer.
7. Press ENTER.
8. When the value stops changing, press ENTER.
9. Press F1.
10. Press DISPLAY to take pH readings.
11. Rinse off the electrode with distilled water and wipe with a kimwipe before returning it to the storage bottle or taking pH measurements.

#### **Using the pH electrode**

1. Rinse your electrode with distilled water and wipe off electrode with a kimwipe both before and after each reading. Be especially careful not to bump the glass bulb on the bottom. It is very fragile and the pH electrode is expensive. **You will be charged for the electrode if it is broken.**
2. Return the electrode to the storage bottle between readings and when you are finished with the experiment. **Be sure the cap is screwed on tightly to the storage bottle to prevent leaking. Do not remove the cap from the electrode. Always unscrew the cap from the storage bottle before use.**
3. Press ON/OFF on the MeasureNet station when you are done with your experiment.
4. Be sure the pH electrode is upright in the storage bottle before leaving the lab.
5. Be sure that the bulb on the pH meter is covered with solution when the electrode is returned to the storage bottle.

## 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.

## Experimental Procedure

**Your TA must sign your data before leaving lab or you will not receive credit for attending the lab. Each person must run this test individually. Partners should then check their data against each other for consistency. Repeat the experiment if there is a large variation between pH values for the same solution number.**

1. Record the exact concentration of the sodium hydroxide from the board in your laboratory notebook.
2. 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 8.0 mL of acid. Fill the 25 mL volumetric to the line with distilled water and swirl to mix.
4. Pour the solution into a 30mL beaker.
5. Calibrate your pH meter with the pH 7 buffer.
6. Once calibrated, rinse off the bulb of the pH meter with distilled water and then insert the pH meter into the beaker containing the acid/base mixture.
7. Gently stir the solution with the pH meter and watch the reading. When the reading has stabilized on the pH meter, record the value in your lab notebook.
8. Rinse the pH meter with distilled water and return it to the buffer solution.
9. Empty your solution into the waste container and rinse your volumetric flask out well with distilled water.
10. Repeat this procedure for the remaining 3 solutions given in the table below.

<b>Solution number</b>	<b>Volume of 1.00M weak acid mL</b>	<b>Volume of 0.5M NaOH mL</b>
1	8.00	2.50
2	8.00	5.00
3	8.00	7.50
4	8.00	10.00

### Cleanup

1. Dispose of solutions in the waste container provided.
2. Rinse all glassware with distilled water and remove markings with acetone if necessary.

## Laboratory Data

Record the data shown during lab in pen.

Include the **signed** white copy of this data when you turn in your lab report.

Include the correct number of significant figures and the units for each measurement.

### Data

Concentration of Stock Acid Solution \_\_\_\_\_

Concentration of Stock NaOH Solution \_\_\_\_\_

**Table 1: pH of Strong Base/Weak Acid Solutions**

Solution Number	mL Acid	mL Base	pH
1	8.00	2.50	
2	8.00	5.00	
3	8.00	7.50	
4	8.00	10.00	

## Laboratory Results

Create a typed table with the following results

Include the correct number of significant figures and the units for each measurement.

**Table 2:  $K_a$  Calculations**

Solution Number	1	2	3	4
$[H_3O^+]$ , (x)				
$M_{dil. acid}$				
$M_{dil. NaOH}$				
$HA_{ICE}$				
$A^-_{ICE}$				
$H_3O^+_{eq}$				
$HA_{eq}$				
$A^-_{eq}$				
$K_a$				

Average  $K_a$  \_\_\_\_\_

Identity of Weak Acid \_\_\_\_\_

## Data Sheet; Chemistry 114: Experiment 5

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

TA Signature: \_\_\_\_\_

### Table 1



## Calculations

Remember to show 1 example of each calculation either handwritten or typed on a separate sheet.

Include correct significant figures and units

Units can be included in column or row title as demonstrated in tables below

Brackets, [xx], can be used to designate concentration in molarity.

Include a typed copy of these results in a table with your lab report.

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

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

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

### **Concentration of Diluted Weak Acid Before the Addition of NaOH, $M_{dil. acid}$**

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 volume of the volumetric flask which is also the total volume of the dilute acid.

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

### **Concentration of Diluted NaOH, $M_{dil. NaOH}$**

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 volume of the volumetric flask which is also the total volume of the dilute NaOH.

$$M_{dil. NaOH} = \frac{M_{conc. NaOH} V_{conc. NaOH}}{V_{NaOH}}$$

### **Concentration of Diluted Weak Acid After the Addition of NaOH, $HA_{ICE}$**

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, you account for the addition of the NaOH by subtracting the concentration of the diluted NaOH from the concentration of the diluted weak acid before the addition of the NaOH.



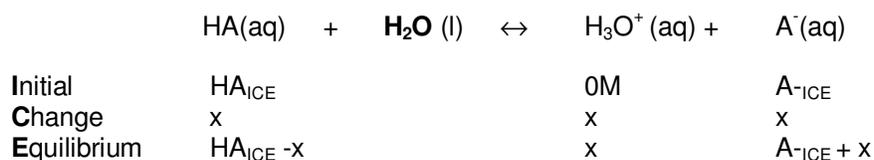
$$M_{acid \text{ in ICE table}} = M_{dil. Acid} - M_{dil. NaOH}$$

### **Concentration of Weak Base, $A^-_{ICE}$**

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

### ICE Tables

Set up 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.



### Equilibrium Concentrations, $\text{H}_3\text{O}^+_{\text{eq}}$ , $\text{HA}_{\text{eq}}$ , and $\text{A}^-_{\text{eq}}$

$\text{H}_3\text{O}^+_{\text{eq}}$  is the concentration of  $\text{H}_3\text{O}^+$  found from the pH in the first calculation.

$\text{HA}_{\text{eq}}$  is the HA concentration initially calculated for the ICE table minus the  $\text{H}_3\text{O}^+_{\text{eq}}$  concentration.

$\text{A}^-_{\text{eq}}$  is the A<sup>-</sup> concentration initially calculated for the ICE table plus the  $\text{H}_3\text{O}^+_{\text{eq}}$  concentration.

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

### Calculation of $K_a$

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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[x][\text{A}^-_{\text{eq}}]}{[\text{HA}_{\text{eq}}]}$$

### 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 the table below and record the identity of the weak acid.

Table 1

Substance	Formula	$K_a$ at 25°C
Iodic acid	$\text{HIO}_3$	$2.0 \times 10^{-1}$
Chlorous acid	$\text{HClO}_2$	$1.0 \times 10^{-2}$
Nitrous acid	$\text{HNO}_2$	$1.0 \times 10^{-3}$
Formic acid	$\text{HCHO}_2$	$2.0 \times 10^{-4}$
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	$2.0 \times 10^{-5}$
Hypochlorous acid	$\text{HOCl}$	$5.0 \times 10^{-8}$
Hypobromous acid	$\text{HOBr}$	$2.0 \times 10^{-9}$
Hydrocyanic acid	$\text{HCN}$	$5.0 \times 10^{-10}$
Hypoiodous acid	$\text{HOI}$	$2.0 \times 10^{-11}$

## Discussion Questions

**You must use your data to answer these questions. If the answer you give does not reflect YOUR data and results, you will receive no credit for the question.**

1. Create a table of pK<sub>a</sub> values for each of the acids listed in Table 1. Calculate the pK<sub>a</sub> value for your acid from the average K<sub>a</sub> value you calculated in the results section. (pK<sub>a</sub> = -logK<sub>a</sub>). Which acid best matched your pK<sub>a</sub> value?
2. Calculate your percent error using your calculated pK<sub>a</sub> value as your experimental value and the actual pK<sub>a</sub> of the acid you selected from the table you generated from question 1. Are you confident in the identification of your acid? Why or why not?

$$\%Error = \frac{|Experimental\ pK_a - Actual\ pK_a|}{Actual\ pK_a} \times 100$$

3. What would be the result if you added an amount of NaOH that exceeded the amount of your weak acid in the diluted acid solution? Explain how you would calculate the pH of the solution.
4. The values for the dissociation equilibrium constants are recorded in the table at 25°C. What do you expect to see in terms of a change in K<sub>a</sub> if the temperature were increased? Explain your reasoning.
5. How would your values of K<sub>a</sub> change if you accidentally calibrated your pH meter to read 7.0 when the actual pH of the solution was 10.0? You don't need to do any calculations, just explain whether the K<sub>a</sub> would be higher or lower and why.

## Prelab 5 Chem 114

Name: \_\_\_\_\_

Section#: \_\_\_\_\_

Show work to support answers

You make a solution with a pH of 3.2 and the  $K_a$  is  $1.0 \times 10^{-4}$ .

1. Is the solution acidic or basic?
2. Calculate the  $[H_3O^+]$ .
3. Calculate the pOH.
4. Calculate the  $[OH^-]$ .
5. Calculate the  $pK_b$ .
6. Calculate the  $K_b$ .

For a solution of an aqueous formic acid solution if the  $K_a = 1 \times 10^{-4}$  and  $[HCOOH] = 0.20M$ ?

7. Calculate the pH of this solution.
8. If you add 0.05M NaOH to the solution, what is the new concentration of  $[HCOOH]$ ?

You make 100.00mL of a 0.15M solution of NaOH from a 2.0M stock solution.

9. How many milliliters of the concentrated stock solution will you need?
10. What is the pH of the diluted solution?

## Experiment Checklist: This sheet must be attached to your lab report

### Points:

_____	Format (in order) (0 / 5)	5pts	Each numbered section should be on separate page(s), unless otherwise noted. Typed in size 10 font, single spaced, headings: size 12 font (1) Title page: Title, Name, TA name, Course, section and date (2) Purpose and procedure: Both should be on 1 single page (3) Original Data: Must have TA signature, handwritten in lab (4) Sample Calculations: May be handwritten (5) Results Table: Typed table (6) Discussion Questions (7) Conclusions (8) Experiment checklist: Last page in each experimental write-up
_____	Purpose (0 / 5)	5pts	Paragraph of complete sentences <b>summarizing</b> purpose of experiment Must include a clear explanation of what was learned in experiment
_____	Procedure (0 / 5)	5pts	Full procedure not needed, just any changes to experimental procedures (1) Give experiment title and page (s) of instructions: ex: Buffers: Pg. 4-5 (2) Heading of each portion of experiment: ex: Part 1: Making a dilution (3) Under each heading note changes and line of experiment where changed (4) Note why each change was made, if no changes, state "no changes made"
_____	Data (0 / 5) (0 / 5) (0 / 5) (0 / 5)	20pts	Original data sheet must have TA signature or 50 pt deduction _____ All data required in the lab is recorded _____ Observations are recorded during the experiment _____ Data is neat and legible _____ Data is in tables as described in the lab manual
_____	Calculations (0 -15 sliding)	15pts	Calculations can be hand written. Only 1 sample calculation is required. _____ All calculations listed in experiment are present and correct _____ Calculations must be labeled with the headings given in the calculation section
_____	Results (0 / 5 / 10)	10pts	<i>Typed tables</i> with <u>all</u> results. Must match calculations from original data _____ Incorrect results: do not match calculations _____ Correct significant figures and units are included with all values _____ Results must be labeled with the headings given in the calculation section
_____	Discussion Questions (0 / 3 / 6) X 5	30pts	Answers must be typed and in complete sentences. Q1 _____ Q2 _____ Q3 _____ Q4 _____ Q5 _____
_____	Conclusions (0 / 5 / 10)	10pts	5 - 10 complete sentences typed in paragraph form <b>IN YOUR OWN WORDS</b> _____ Error sources are specific to experiment _____ Discrepancies between data collected and expected results are explained _____ Clear final sentence about success in relation to purpose of experiment
<b>Deductions:</b>			_____ Checklist missing: -10 pts _____ Original data sheet missing -50pts _____ Significant figures are incorrect in data and/or results -5pts _____ Units are missing from data and/or results -5pts _____ Calculations not performed with data from data sheet: -50 pts _____ Lab report is not typed (original data& calculations can be handwritten) -20pts _____ Plagiarism (copying from another source): -100 pts _____ Lab technique points: up to 20pt deduction at your TAs discretion _____ Late or unprepared _____ Lab area not clean _____ Improper waste disposal _____ Disruptive behavior
_____	Total Score	100pts	