### Determination of the Molar Mass and Ionization Constant of a Weak Acid

### Pre-Laboratory Assignment

Complete these exercises after reading the experiment but before coming to the laboratory to do it.

An aqueous solution of propionic acid, CH<sub>3</sub>CH<sub>2</sub>COOH, is prepared in the laboratory by dissolving 3.6 g of the acid in a liter of solution. In a titration of this acid with an aqueous solution of NaOH, 25.00 mL of the acid required 12.15 mL of a 0.100 M aqueous NaOH solution for complete neutralization using phenolphthalein as indicator.

- 1. How many moles of NaOH are required to completely react with the 25.00 mL aliquot of the acid?
- What is the molarity of the propionic acid solution given that the following equation represents the reaction:
  CH<sub>3</sub>CH<sub>2</sub>COOH(aq) + NaOH(aq) → NaCH<sub>3</sub>CH<sub>2</sub>COO(aq) + H<sub>2</sub>O(*I*)
- 3. What is the molar mass of the acid expressed in g/mol?
- 4. In a titration of the above propionic acid solution with the 0.100 M NaOH, a student added 6.10 mL of the NaOH solution to the acid, stopped at that point, and used a calibrated pH meter to check the pH of the resulting solution, and found it to be 4.88.

What will be  $K_a$ , the acid dissociation equilibrium constant, for propionic acid? Show your reasoning.

### Determination of the Molar Mass and Ionization Constant of a Weak Acid

#### PURPOSE

To determine the molar mass and acid dissociation constant of acetic acid (a weak monoprotic acid) by titration and pH measurement of solutions containing a known mass concentration of acetic acid. To determine the molar mass and acid ionization constant of an unknown weak acid. To learn how to use a pH meter to measure the pH of a solution.

#### **PRE-LAB PREPARATION**

Acids and bases are important classes of chemical compounds. They control the pH of living systems and of many reactions carried out in the chemical laboratory. If the pH of the blood of most animals shifts by as little as 0.3 units above or below the normal range of 7.3 to 7.5, severe illness results. Therefore, if we understand the principles of how acids and bases function, we will be better informed about the functioning of biological systems, as well as of general chemical systems.

In this experiment we will study the properties of weak acids that can ionize (dissociate) by reaction with water to yield one hydronium ion (a protonated water molecule,  $H_3O^+$ ). Such acids are called weak monoprotic acids. Acetic acid, the active ingredient in vinegar, is a common weak acid belonging to this class. We will determine its molar mass by titration and its ionization constant by making measurements of pure acetic acid. We can also apply exactly the same principles to determine the molar mass and ionization constant of an unknown weak monoprotic acid.

Acetic acid has the molecular formula

$$H - C - C + C + O - H$$

The molecular formula for acetic acid is generally shortened to read  $CH_3COOH$  or  $HC_2H_3O_2$ . These chem-

ical formulas are often further abbreviated to HA, where HA represents acetic acid (or any generic weak monoprotic acid). Then the symbol  $A^-$  stands for acetate ion,  $CH_3CO_2^-$ , the anion of acetic acid (or the anion of any weak monoprotic acid, HA).

The proton that dissociates in acetic acid is the one attached to the oxygen atom. The O–H bond in the acetic acid molecule is appreciably weaker than the C–H bonds, and the polarity of the O–H bond makes it easier for the proton to transfer to a water molecule. In contrast to the behavior of hydrogen atoms bonded to oxygen, there is no significant ionization of the hydrogen atoms bonded to carbon in aqueous solution.

Acetic acid ionizes according to the equation

$$HA + H_2O = H_3O^+ + A^-$$
(1)

The equilibrium constant expression is given by

$$K_{a} = \frac{[H_{3}O^{+}][A^{-}]}{[HA]}$$
(2)

The literature value of the equilibrium constant for this reaction is  $1.76 \times 10^{-5}$  at  $25^{\circ}$ C.<sup>1</sup> You are to measure the value of this constant in this experiment and compare your value with the literature value.

A straightforward way to obtain the value of  $K_a$  is to measure each of the quantities on the right-hand side of Equation (2) and carry out the indicated arithmetic. For solutions containing only the weak acid HA, the value of  $K_a$  can be determined by examining the ionization reaction shown in Equation (1) and noting that the concentration of A<sup>-</sup> will be equal to that of the H<sub>3</sub>O<sup>+</sup> (ignoring the insignificant amount of H<sub>3</sub>O<sup>+</sup> that comes from the ionization of

<sup>&</sup>lt;sup>1</sup> This is the value of  $K_a$ , obtained by extrapolating to zero ionic strength. In any real solution of acetic acid, the ionic strength is greater than zero, and the dissociation constant is somewhat larger because of electrostatic interactions between the ions in solution. (Harris Chapter 8)

water). The HA concentration in the solution is equal to the *stoichiometric* concentration of HA in the solution minus the amount of HA lost by ionization.<sup>2</sup> For acetic acid and most other weak acids, the amount of HA lost by ionization is much smaller than the amount put into solution and thus the equilibrium concentration of HA is only slightly smaller than the stoichiometric concentration.

In solutions that contain both acetic acid (HA) and sodium acetate (Na<sup>+</sup>A<sup>-</sup>), we will show that the equilibrium concentrations of HA and A<sup>-</sup> are approximately equal to their stoichiometric concentrations. (Similar conclusions will apply to any solution containing a mixture of a weak monoprotic acid, HA, and its salt, Na<sup>+</sup>A<sup>-</sup>.) The stoichiometric concentrations can be readily determined by titration or by knowledge of the quantities of HA and Na<sup>+</sup>A<sup>-</sup> used to prepare the solutions. If we know the stoichiometric concentrations are equal to the stoichiometric concentrations, in order to determine  $K_a$ , all that remains is to calculate the [H<sub>3</sub>O<sup>+</sup>] from the measured pH.

$$pH = -log[H_3O^+]; [H_3O^+] = 10^{-pH}$$
 (3)

#### MEASURING THE TOTAL ACID CONCENTRATION BY TITRATION

To determine the molar mass of acetic acid, one of the things we need to know is the total amount of acid present in the original sample solution. This can be readily determined by titration of the acetic acid with a strong base of known concentration, such as sodium hydroxide. An acid-base indicator or a pH meter can be used to determine the endpoint of the titration. Figure 1 helps to explain how the titration works. It shows how the pH of the solution changes as a strong base, NaOH, is added to the solution containing the weak monoprotic acid.

After an initial small rise in pH, the pH does not change very rapidly as NaOH is added. In the middle of the titration, there is an appreciable concentration of both HA and  $A^-$  present, so adding a small amount of base (or acid) does not change the pH very much. For this reason, this is called the *buffering* region.

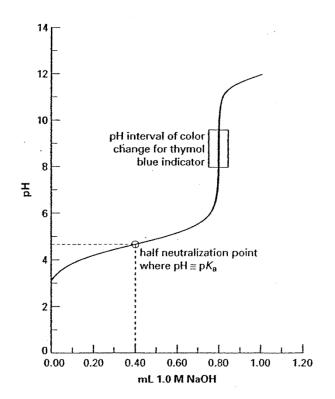
When an amount of NaOH equivalent to the amount of acid has been added, the concentration of  $H_3O^+$  decreases very sharply with a corresponding sharp

increase in the pH. This is the endpoint of the titration, where the indicator changes color. The pH interval of the color change of the indicator must be a good match to the pH at the endpoint as shown in Figure 1.

## DETERMINING K<sub>a</sub> BY THE METHOD OF HALF-NEUTRALIZATION

At exactly the midpoint of the titration when half of the acid has been neutralized, there will be equal amounts of HA and A<sup>-</sup> in solution. This relationship is a good approximation, subject to the condition that [HA] and [A<sup>-</sup>] are both greater than 100 $K_a$ , as discussed in greater detail later. From equation (2) we see that when [HA] = [A<sup>-</sup>], the two terms will cancel so that  $K_a = [H_3O^+]$  and  $pK_a = pH$  at the midpoint of the titration. This provides a simple way to measure the  $pK_a$  of a weak acid. If we have a half-neutralized solution of weak acid, the pH of the solution will be equal to the  $pK_a$  of the acid.  $K_a$  and  $pK_a$  are related like [H<sub>3</sub>O<sup>+</sup>] and pH.

$$pK_a = -\log(K_a); \quad K_a = 10^{-pK_a}$$
 (4)



#### FIGURE 1

Titration of a weak acid with a strong base. The figure shows the titration of 20 mL of 0.04 M acetic acid with 1.0 M NaOH. Thymol blue is a satisfactory acid-base indicator for this titration.

<sup>&</sup>lt;sup>2</sup> The stoichiometric concentrations of HA and A<sup>-</sup> are determined from the amounts of each substance that are put into the solution. However, HA and A<sup>-</sup> can each react with water: HA + HOH  $\longrightarrow$  A<sup>-</sup> + H<sub>3</sub>O<sup>+</sup> and A<sup>-</sup> + HOH  $\longrightarrow$  HA + OH<sup>-</sup>. Therefore, in general the actual concentrations of HA and A<sup>-</sup> at equilibrium (which we will call the equilibrium concentrations) may not be exactly equal to the stoichiometric concentrations.

## DETERMINING THE MOLAR MASS OF A WEAK MONOPROTIC ACID

If we know the mass concentration of acid in units of grams HA/L, it is a straightforward procedure to determine the molar mass of the acid (grams HA/mol). We know that the molar mass of HA has units of grams/mol. If we know the concentration of HA in grams/L, then clearly we have to divide this quantity by mol HA/L (or mmol HA/mL) to get the molar mass.

If we take a known volume of HA solution, we can determine the total amount of HA in the sample by titration with a strong base of known concentration. Then, knowing the volume of the original sample (L) and the total amount of HA (moles), we have the necessary information to complete the calculation of the molar mass:

Molar mass 
$$= \frac{g \text{ HA}}{Liter} \times \frac{Liter}{mole \text{ HA}} = \frac{g \text{ HA}}{mole}$$
 (5)

In a solution of HA and Na<sup>+</sup>A<sup>-</sup>, the equilibrium concentrations of HA and A<sup>-</sup> are approximately equal to their stoichiometric concentrations. By adding sodium hydroxide to a larger amount of a weak acid, we can form a mixture of the weak acid, HA, and its salt, Na<sup>+</sup>A<sup>-</sup>. To determine the  $K_a$  of the weak acid, we must be able to calculate the equilibrium concentrations of HA, A<sup>-</sup>, and H<sub>3</sub>O<sup>+</sup>. In this section we will show how to calculate the stoichiometric concentrations of HA and A<sup>-</sup>. We will then show the equilibrium concentrations are usually equal to the stoichiometric concentrations. In the following section we will discuss how to determine the H<sub>3</sub>O<sup>+</sup> concentration by using a pH meter.

To see how we can determine the stoichiometric concentrations of the acid HA and the base  $A^-$ , let's suppose that we add a known amount of NaOH to a solution containing a larger (and known) amount of HA. The reaction is:

$$HA + Na^{+} + OH^{-} \rightarrow Na^{+} + A^{-} + H_2O$$
 (6)

(The Na<sup>+</sup> ion, which appears on both sides of Equation (6), is simply a spectator ion.)

The *stoichiometric* amount of sodium acetate  $(Na^{+}A^{-})$  formed is equivalent to the amount of NaOH added.

$$mol Na^{+}A^{-}_{formed} = mol NaOH_{added}$$
(7)

The stoichiometric amount of HA left in solution is obtained easily by subtracting the amount of NaOH added from the original amount of HA present in the solution.

$$mol HA_{final} = mol HA_{original} - mol NaOH_{added}$$
 (8)

The stoichiometric composition of the solution is precisely the same as would be obtained if we dissolved the same number of moles of acetic acid and sodium acetate as calculated from Equations (5) and (6) and in the same total volume. This is why these concentrations are called stoichiometric concentrations.

#### HARRIS SYSTEMATIC APPROACH TO EQUILIBRIUM – CHARGE AND MASS BALANCE (text 8.4)

Now let's see how the equilibrium concentrations of HA and A<sup>-</sup> are related to their stoichiometric concentrations. We will represent these stoichiometric concentrations by a subscript zero:  $[HA]_0$  and  $[A^-]_0$ . We will make use of two equations, one based on a *material balance* and the other based on a *charge balance* condition.

First we write the *material balance* equation that expresses the condition that the sum of the stoichiometric concentrations must equal the sum of the equilibrium concentrations:

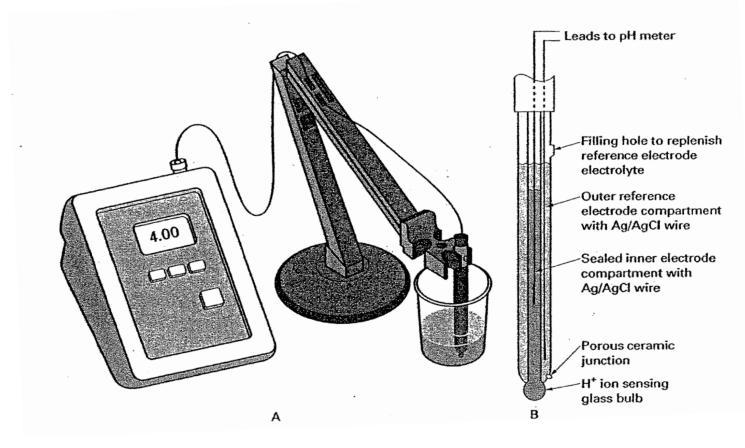
$$[HA]_{o} + [A^{-}]_{o} = [HA] + [A^{-}]$$
(9)

This equation says that if we put known stoichiometric amounts of HA and A<sup>-</sup> in solution, the sum of the stoichiometric concentrations will be exactly equal to the sum of the equilibrium concentrations. This is true because any HA that reacts with water produces A<sup>-</sup> and vice versa, as shown by the equations in footnote 2.

The *charge balance* equation expresses the condition that the sum of the positive charges must equal the sum of the negative charges. This is true because the solution as a whole is electrically neutral. (The charge balance equation includes all of the ions in solution, including those that come from the ionization of water.)<sup>3</sup> The charge balance equation for a solution containing HA and Na<sup>+</sup>A<sup>-</sup> dissolved in water is written as:

$$[Na^{+}] + [H_{3}O^{+}] = [A^{-}] + [OH^{-}]$$
(10)

<sup>&</sup>lt;sup>3</sup> In the charge balance equation, the concentrations of  $H_3O^+$  and  $OH^$ include the contributions from all sources, both from the ionization of water and the reaction of HA and A<sup>-</sup> with water. However, we don't need to worry about keeping separate account of ions coming from water and ions coming from the acid and its salt if they are the same kind of ions. There is only one equilibrium concentration of  $H_3O^+$  and one equilibrium concentration of  $OH^-$  in solution, no matter where they came from.



#### **FIGURE 2**

Figure A shows a typical pH meter while measuring the pH of a beaker of acid (note the pH). Figure B shows how a typical pH probe is constructed.

The stoichiometric concentration of  $A^-$  is exactly equal to the concentration of  $Na^+$ :

$$[A^{-}]_{0} = [Na^{+}] \tag{11}$$

This is the same as saying that each mole of NaOH added to a solution containing a larger amount of HA produces a stoichiometric amount of sodium acetate given by Equation (7). Substituting  $[A^-]_0$  for  $[Na^+]$  in Equation (10) gives:

$$[A^{-}]_{0} + [H_{3}O^{+}] = [A^{-}] + [OH^{-}]$$
(12)

This result shows that the equilibrium concentration of  $A^-$  is equal to the stoichiometric concentration of  $A^-$ , provided that the concentrations of  $H_3O^+$  and  $OH^-$  are negligible compared to the concentration of  $A^-$ . From Equation (9) we see that if  $[A^-]_0$  and  $[A^-]$  are equal,  $[HA]_0$  must equal [HA]. This illustrates the general rule that for a solution containing a mixture of HA and

Na<sup>+</sup>A<sup>-</sup>, the equilibrium concentrations of A<sup>-</sup> and HA will be equal to the stoichiometric amounts of A<sup>-</sup> and HA calculated from equations (7) and (8) (and divided by the total solution volume) provided that HA is not too strong an acid or its concentration too dilute. As a good rule of thumb, this rule will apply whenever the stoichiometric concentrations of HA and A<sup>-</sup> are both greater than  $100K_a$ .

#### USING A pH METER TO MEASURE pH

All pH meters operate by measuring the voltage of an electrochemical cell. The cell is comprised of two half-cell electrodes: a glass-membrane electrode sensitive to the hydrogen ion concentration and a reference electrode.<sup>4</sup> (See Figure 2) The reference

<sup>&</sup>lt;sup>4</sup> Some newer types of pH meters employ a solid state hydrogen ion sensor rather than one based on a glass membrane. The solid state electrodes have the advantage of being more rugged.

electrode is often a silver-silver chloride electrode. Usually the two half-cell electrodes are combined in a single probe unit called a *combination electrode*. The principle of operation, however, is the same for either type. The silver-silver chloride electrode supplies a constant potential ( $E^0 = +0.20$  V vs. the standard hydrogen electrode) determined by the half-reaction

$$AgCl(s) + e^{-} \implies Ag(s) + Cl^{-}(3.5 M)$$
 (13)

The  $[H_3O^+]$  in the solution determines the potential of the glass electrode. The potential (or voltage) developed across the glass membrane is proportional to the logarithm of the H<sub>3</sub>O<sup>+</sup> concentration ratio inside and outside the glass electrode. The pH meter measures the total cell potential across the two half-cell electrodes and displays the measurements on the scale calibrated in pH units (a logarithmic scale, as shown by Equation [3]). When properly standardized with buffers of known pH, a pH meter provides an accurate and simple method for determining the pH of a solution. In Figure 2, note the construction details of the combination glass electrode. The thin glass bulb of the glass electrode and is often protected by a plastic guard. Be extremely careful not to hit the glass bulb against the side or bottom of a beaker.

#### **EXPERIMENTAL PROCEDURE**

1. MEASUREMENT OF pH AND TITRATION OF ACETIC ACID SOLUTION. Your instructor will demonstrate the use of the pH meter. Use 30-mL polyethylene beakers, if available, for holding the samples. Use a wash bottle to rinse the electrode(s) between samples. Excess water can be removed by gently blotting the bulb with a tissue. (Do not rub the bulb.)

Obtain 80 mL of 2.4 g/L acetic acid, 75 mL of standardized 0.10 M NaOH, and a 25- or 50-mL buret. Rinse and fill the buret with 0.10 M NaOH, taking care to expel any bubbles from the tip of the buret. Record the initial volume reading.

Pour 20 mL of the 2.4 g/L acetic acid solution into a clean 30-mL polyethylene beaker. Measure and record the pH. Then transfer the solution to a tared (or weighed) 125-ml Erlenmeyer flask. Add more 2.4 g/L acetic acid and, using a polyethylene transfer pipet, adjust the mass of solution in the flask to  $30.0 \pm 0.1$  g. Record the mass of the sample. Add 5 drops of 0.1% thymol blue indicator. Titrate the sample of acid to the first

appearance of a permanent blue color. Record the final volume reading of the buret.

Repeat the pH measurement and titration with a second 30.0-g sample of 2.4 g/L acetic acid. For each sample calculate the mmole of acid/mL sample. (Assume that each 1.00 g of sample = mL.) Average the values for the two samples. If they do not agree within 5 percent, titrate a third sample, and average all three samples. Also average the pH values measured for each sample before they were titrated.

**Calculations.** Calculate the molar concentration of the 2.4 g/L acetic acid (mmole acid/mL of acid) from the average volume of NaOH required to titrate the samples of acetic acid. Calculate the molar mass of acetic acid (g/mol) Equation (5). Compare with the expected molar mass for acetic acid whose molecular formula is CH<sub>3</sub>COOH.

Using the average molar concentration and average pH, calculate the ionization constant for acetic acid. Compare this value with the literature value and with the value measured by the halfneutralization method.

2. MEASUREMENT OF THE pK<sub>a</sub> OF ACETIC ACID BY THE **HALF-NEUTRIZATION** METHOD. Weigh into a clean tared Erlenmeyer flask the same size sample of 2.4 g/L acetic acid that you used in Part 1. Add to the flask exactly half of the average volume of NaOH required to titrate the sample, following the procedure you used in Part 1. Mix thoroughly. This will produce a solution of acetic acid that is exactly half-neutralized. Measure and record the pH of this solution. If the pH meter is properly calibrated, the pH will be equal, to a good approximation, to the  $pK_a$  of the acid, as was shown in the Pre-Lab Preparation.

**3. THE MOLAR MASS AND IONIZATION CONSTANT OF AN UNKNOWN WEAK MONOPROTIC ACID.** You will be provided with aqueous solutions of an unknown acid, identified only by its mass concentration (g/L). Following the same procedure used in parts 1 and 2, determine the molar mass and ionization constant for the weak monoprotic acid. Assuming the acid is a carboxylic acid of the general formula RCOOH, try to identify the acid from the list of acids given in the table posted on the wall of the lab.

# Consider This (You are not responsible for this section)

In the method of half-neutralization for the measurement of the  $pK_a$  of an acid, we assume that the equilibrium concentrations of  $A^-$  and HA are equal to their stoichiometric concentrations. In order for this to be true,  $[H_3O^+]$  and  $[OH^-]$  must be negligibly small compared to  $[A^-]$ . Show that this condition is fulfilled in the measurements you made in Part 2.

By taking the logarithm (base 10) of both sides of Equation (2) and multiplying all of the terms by -1 we can obtain the following equation:

$$-\log(K_a) = -\log[H_3O^+] - \log \frac{[A^-]}{[HA]}$$
 (14)

which is equivalent to

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$
(15)

Now if we added 5 percent more than the calculated volume of NaOH required to half-neutralized an acid, the ratio of  $[A^-]/[HA]$  would be approximately equal to 1.05/0.95. Show from Equation (15) that this would cause the measured pH to be 0.04 units larger than if we added the exact amount required. This is probably a fairly realistic estimate of the uncertainty in our measured value of  $pK_a$ .

In making the comparison of the ionization constants that you measured with literature values, you should be aware that the interionic attraction effect causes the value of  $K_a$  for the solutions used in this experiment to increase (and  $pK_a$  to decrease) as the concentration of the ions in solution increases. In brief, the electrostatic attraction of oppositely charged ions act to decrease the effective concentrations (called the activity) of the ions in the solution. This causes the ionization constants for weak monoprotic acids of the types we are studying in this experiment to increase by about 15 percent at an ionic strength of 0.02 M. Values of ionization constants tabulated in the literature have usually been determined by extrapolating to zero ionic strength, where interionic attraction effects are be negligible.

REPORT	Determination of the Molar Mass and	NAME	
	Ionization Constant of a Weak Monoprotic		
	Acid	SECTION	LOCKER
1()			
		INSTRUCTOR	DATE

#### DATA AND CALCULATIONS

#### 1. Measurement of pH and Titration of Acetic Acid Solution

Concentration of standardized NaOH titrant \_\_\_\_\_ mol/L

Mass concentration of acetic acid \_\_\_\_\_ g/L

	Trial 1	Trial 2	Trial 3
Measured pH of the acetic acid solution			
Mass of acetic solution taken for titration, g			
Initial buret reading of NaOH titrant, mL			
Final buret reading of NaOH titrant, mL			
Net volume of NaOH, mL			
Millimoles of NaOH to endpoint of titration, mmol			
Millimoles of acetic acid in sample, mmol			
Molar concentration of acetic acid solution, mol/L			
Calculated molar mass of acetic acid, g/mol			

#### Calculation of the ionization constant for acetic acid from the measured pH of the acetic acid samples

(Average the pH and molar concentration values for the samples of acetic acid you titrated; used the average values in the calculation of the ionization constant.)

(a) Average molar concentration of acetic acid for the samples you titrated: \_\_\_\_\_ mol/L

Average pH \_\_\_\_\_

Calculate the corresponding  $[H_3O^+]$ , compute the concentration of A<sup>-</sup> and HA, and calculate the dissociation constant,  $K_a$ .

\_\_\_\_\_ M H<sub>3</sub>O<sup>+</sup>

\_\_\_\_\_ M A-

\_\_\_\_\_ M HA

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

Determination of the Molar Mass and Ionization Constant of a Weak Acid

#### 2. Measurement of the pKa of Acetic Acid by the Half-Neutralization Method

Concentration of standardized NaOH titrant \_\_\_\_\_ mole/L

	Trial 1	Trial 2	Trial 3
Mass of acetic acid solution, g			
Volume of NaOH added to half-neutralize the acetic acid, mL			
Measured pH of half-neutralized solution			
Average pH value $pK_a = \; \qquad K_a = \;$		ad activities	
Calculate the $[H_3O^+]$ and the concentrations of A <sup>-</sup> and HA, (Note: In this solution, $[H_3O^+] \neq [A^-]$ )	in the nan-neutranze	a solution	
M H <sub>3</sub> O <sup>+</sup>	M A-		М НА
3. The Molar Mass and Ionization Constant of an Unknow	n Weak Monoproti	c Acid	
Concentration of standardized NaOH titrant	mol/L		
Mass concentration of unknown weak monoprotic acid	g/L		
	Trial 1		Trial 2
Measured pH of the unknown acid solution			
Mass of unknown acid solution taken for titration, g			
Initial buret reading of NaOH titrant, mL			
Final buret reading of NaOH titrant, mL			
Net volume of NaOH, mL			
Millimoles of NaOH to endpoint of titration, mmol			
Millimoles of unknown acid in sample, mmol			
Molar concentration of unknown acid in solution, mol/L			
Calculated molar mass of unknown acid, g/mol			

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#### Calculation of the ionization constant for the unknown acid from the measured pH of the unknown acid samples

(Average the pH and molar concentration values for the samples of unknown acid you titrated; use the average values in the calculation of the ionization constant.)

(a) Average molar concentration of unknown for the samples you titrated \_\_\_\_\_ mol/L.

Average pH \_\_\_\_\_

Calculate the corresponding [H<sub>3</sub>O<sup>+</sup>], compute the concentration of A<sup>-</sup> and HA, and calculate the dissociation constant,  $K_a$ .

\_\_\_\_\_ M H<sub>3</sub>O<sup>+</sup>

\_\_\_\_\_ M A-

\_\_\_\_\_ M HA

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

#### Measurement of the pKa of Unknown Acid by the Half-Neutralization Method

Concentration of standardized NaOH titrant \_\_\_\_\_ mole/L

	Trial 1	Trial 2	Trial 3
Mass of unknown acid solution, g			
Volume of NaOH added to half-neutralize the unknown acid, mL			
Measured pH of half-neutralized solution			

Average pH value \_\_\_\_\_

 $pK_a =$ \_\_\_\_;  $K_a =$ \_\_\_\_;

Calculate the  $[H_3O^+]$  and the concentrations of A<sup>-</sup> and HA, in the half-neutralized solution

(Note: In this solution,  $[H_3O^+] \neq [A^-]$ )

\_\_\_\_\_ M H<sub>3</sub>O<sup>+</sup>

\_\_\_\_\_ M A-

\_\_\_\_\_ M HA

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Comparing both the calculated molar mass and the ionization constant, which acid in the list of acids (ask TA if not posted) is the unknown acid mostly likely to be?

Give the molar mass and  $pK_a$  for the unknown acid that you measured:

Give the molar mass and  $K_a$  for the acid that you think is the same as your unknown acid.

**Consider This** (You are not responsible for this section and for the following page) In the method of half-neutralization for the measurement of the  $pK_a$  of an acid, we assume that the equilibrium concentrations of  $A^-$  and HA are equal to their stoichiometric concentrations. In order for this to be true,  $[H_3O^+]$ and  $[OH^-]$  must be negligibly small compared to  $[A^-]$ . Show that this condition is fulfilled in the measurements you made in Part 2.

By taking the logarithm (base 10) of both sides of Equation (2) and multiplying all of the terms by -1 we can obtain the following equation:

$$-\log(K_{a}) = -\log[H_{3}O^{+}] - \log\frac{[A^{-}]}{[HA]}$$
(14)

which is equivalent to

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$
(15)

Now if we added 5 percent more than the calculated volume of NaOH required to half-neutralize an acid, the ratio of  $[A^-]/[HA]$  would be approximately equal to 1.05/0.95. Show from Equation (15) that this would cause the measured pH to be 0.04 unites larger that if we had added the exact amount required. This is probably a fairly realistic estimate of the uncertainty in our measured value of  $pK_a$ .

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The OH<sup>-</sup> concentration of 0.050 M ammonia, NH<sub>3</sub>, is  $9.5 \times 10^{-4}$  M.

(a) Write the chemical equation for the dissociation of  $NH_3$  in water.

(b) Write the equilibrium constant expression for the reaction of NH<sub>3</sub> with water.

(c) Calculate the value of  $K_b$  using the information given.

Calculate the  $H_3O^+$  concentration and pH of a carbonated beverage that is 0.10 M in dissolved CO<sub>2</sub>. (Essentially all of the  $H_3O^+$  comes from the first stage of dissociation,  $CO_2(aq) + 2H_2O \implies H_3O^+ + HCO_3^-$ , for which  $K_1 = 4.4 \times 10^{-7}$ .)

\_\_\_\_\_M

\_\_\_\_\_ pH