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Experiment #9 – pH Measurements, Buffers and Determination of the Equivalent Mass and K_a of an Unknown Weak Acid

One of the more important properties of an aqueous solution is its concentration of hydrogen ion. The H^+ or H_3O^+ ion has great effect on the solubility of many inorganic and organic species, on the nature of complex metallic cations found in solutions, and on the rates of many chemical reactions. It is important that we know how to measure the concentration of hydrogen ion and understand its effect on solution properties.

For convenience, the concentration of H^+ ion is frequently expressed as the pH of the solution rather than as molarity. The pH of a solution is related to $[H^+]$ by the following equations:

$$pH = -\log [H^+] \quad \text{and} \quad [H^+] = 10^{-pH} \qquad (1)$$

Examples: When $[H^+]$ is 1×10^{-4} moles per liter, the pH of the solution is 4. When the $[H^+]$ is 5×10^{-2} M, the pH is 1.3.

Basic solutions can also be described in terms of pH. In aqueous solutions, the following equilibrium relationship exists:

$$[H^+]\,[OH^-] = K_w = 1 \times 10^{-14} \text{ at } 25\ °C \qquad (2)$$

In pure water, $[H^+] = [OH^-]$, so by equation 2, $[H^+] = 1 \times 10^{-7}$ M. Therefore, the pH of pure water is ideally 7. Solutions in which $[H^+] > [OH^-]$ are said to be acidic and will have a pH < 7; if $[H^+] < [OH^-]$, the solution is basic and its pH > 7.

In part 1A of this experiment, you will determine the approximate pH of a liquid unknown solution by using several colorful acid-base indicators and comparing to various buffer solutions. In part 1B you will determine the pH, K_a and % dissociation of several concentrations of acetic acid. Part 2 of the experiment involves predicting the pH of several salt solutions, verifying your predictions using a pH meter, and then writing out hydrolysis equations. In part 3, you will prepare a buffer by half-neutralizing a solution of an unknown weak acid with the strong base NaOH and measure its pH. From the known pH at half equivalence, you will calculate the K_a of the weak acid and then test the buffer's ability to resist change in pH as compared with tap water. In part 4 you will determine the gram equivalent mass (GEM) of a solid unknown acid by titration with a standardized strong base (NaOH). In Part 5 you will use the computerized LabQuest Mini drop counter and pH meter to construct a weak acid/strong base titration curve. From this titration curve data, you will be able to calculate both the gram equivalent mass and the value of the equilibrium constant for the dissociation of the acid, K_a.

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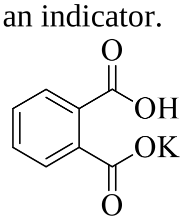
Acids are substances that contain ionizable hydrogen atoms within the molecule. Strong acids ionize completely, weak acids partially. The value of K_a, the equilibrium constant for the dissociation of the acid, is an indication of the strength of the acid. An acid may contain one or more ionizable hydrogen atoms in the molecule. The gram equivalent mass of an acid is the molecular mass divided by the number of ionizable hydrogen atoms in a molecule. For example, hydrochloric acid, HCl, contains one ionizable hydrogen atom; the molecular mass is 36.45 g/mole HCl, and the equivalent mass is also 36.45 g/mole H^+. Sulfuric acid, H_2SO_4, contains two ionizable hydrogen atoms; the molecular mass is 98.07 g/mole H_2SO_4, yet the equivalent mass is 49.04 g/mole H^+. Thus, 36.45 g of HCl or 49.04 g of H_2SO_4 would provide you with one mole of H^+ ions.

The equivalent mass may be determined by titrating an acid with a standardized solution of NaOH. Since one mole of NaOH reacts with one mole of hydrogen ion, at the equivalence point, the following relation holds:

$$V_b \text{ x } M_b = \text{moles base} = \text{moles } H^+$$
$$GEM_a = \text{grams acid/moles } H^+$$

where V_b is the volume of base in liters, M_b is the molarity of base, grams acid is the mass of acid used, and GEM_a is the gram equivalent mass of the acid.

The concentration of the NaOH solution must be accurately known. To "standardize" the NaOH (that is, to find its exact molarity so it becomes a secondary standard), the NaOH is titrated against a solid acid, potassium hydrogen phthalate, sometimes abbreviated KHP (shown below). This acid is chosen because it possesses qualities of a primary standard which include a relatively large molar mass, high purity, unreactive with the atmosphere, one invariable reaction, and soluble in the chosen solvent. Other advantages of using KHP include its affordability, and it is relatively nontoxic compared to other possible choices. Sodium hydroxide cannot be used as a primary solid because it reacts with the atmosphere so it does not remain pure, and it has a relatively low molecular weight. The titration is thus followed using phenolphthalein as an indicator.

KHP or 

or $KHC_8H_4O_4$

A weak acid/strong base titration curve of pH versus mL of NaOH has four distinct areas; a) weak acid at zero ml, b) buffer zone, c) salt at equivalence pt, and d) strong base beyond equivalence. There should be a significant change in pH in the vicinity of the equivalence point. Note that the equivalence point will probably NOT be at pH 7, but will be on the basic side.

The equilibrium equation and the corresponding expression are given below.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad (3)$$
$$K_a = [H_3O^+][A^-] / [HA] \qquad (4)$$

When the acid is HALF neutralized, [HA] = [A^-], so these terms cancel in the equation (4), and K_a = [H_3O^+]. Therefore, when the acid is half-neutralized, pH = pK_a. The value of the equilibrium constant for the dissociation of the acid can be determined from the half equivalence point.

The point where pH is equal to pK_a can be found from the graph. Refer to Figure 1.

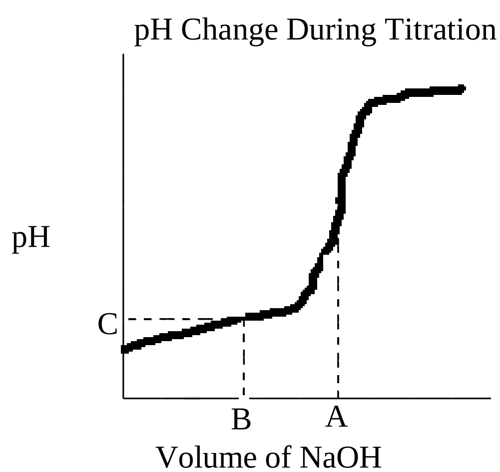


Figure 1. Titration of a Monoprotic Weak Acid with Sodium Hydroxide

In this graph, A = Volume NaOH at equivalence point; B = ½ volume of A or the volume when half-neutralized; and C = pH when half-neutralized, or pK_a.

Safety / Caution: Acids and bases can irritate your skin and eyes. Wear safety goggles during the entire lab. Acid powder spilled on clothing may react with laundry soap (bases) and can cause some holes or torn fibers on clothing.

Procedure

Part 1A: pH of Unknown and Buffer Solutions

1. Obtain a liquid unknown solution and place a drop of the solution onto a small strip of pH paper.

2. Estimate the pH of the liquid unknown solution by comparing the colors of the pH test strip with the color chart on the plastic box of the test strips. The precision of the scale on the box of the pH paper is about $\pm$ 1. So note your estimate in a 3-pH unit range (e.g. estimate pH = 7 – 9).

3. Obtain a spot plate. Place 5 drops of your unknown into 3 wells as seen in Figure 2 below. Obtain three buffer solutions that correspond to your 3-pH unit estimate of your unknown. Place 5 drops of each buffer solutions into 3 wells as indicated in Figure 2.

4. Choose about three indicators that have a useful range that overlaps with most or some of your 3-pH unit range estimate of your unknown. For each indicator, place a drop of one indicator in a well with the unknown and one in each of the three different buffers as seen in Figure 2. Record the colors of each well on the table in Part 1 of Data and Calculations.

5. Use the pH values of the buffers to improve your estimate of the pH of your unknown by looking for the best color-match between your unknown and the buffers. Estimate the pH to the nearest 0.5 pH unit. Record this pH in the space provided below the table in Part 1 of Data and Calculations.

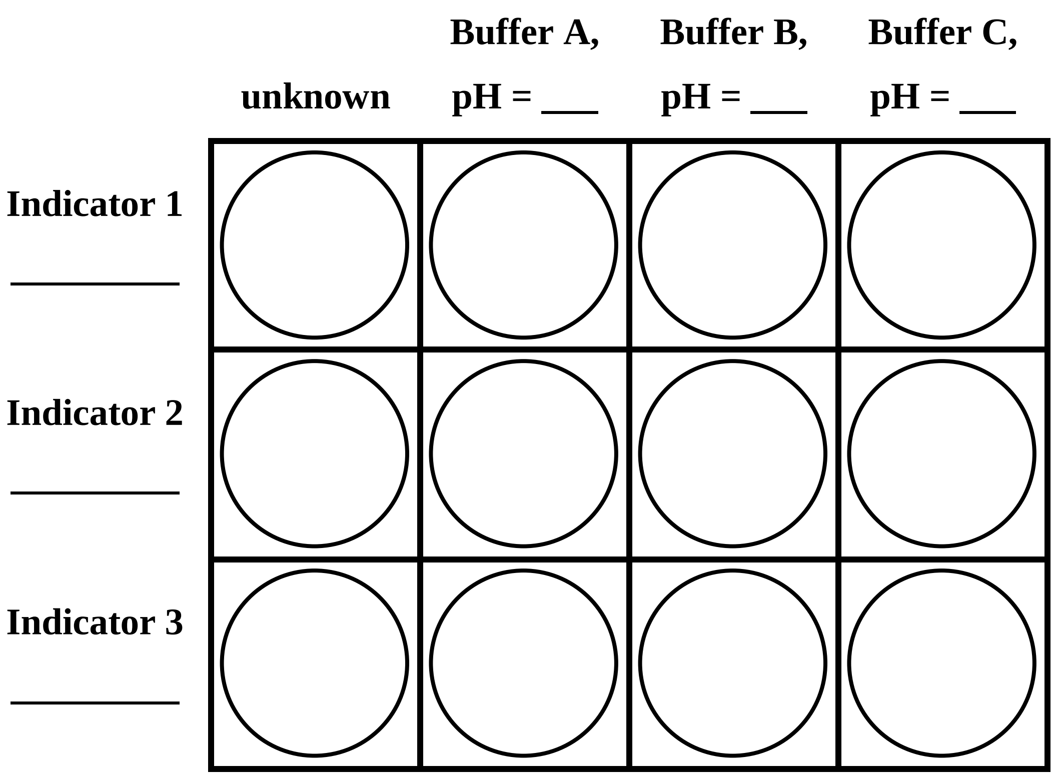


Figure 2. Schematic of first spot plate solution distribution

<u>Part 1B</u>: pH of Acetic Acid Solutions.

1. Record the pH of 1.0 M, 0.10 M and 0.010 M HAc (acetic acid) solutions by reading the three pH meters set up for the class.

2. Calculate the K_a and % dissociation of HAc using these three pH measurements. Show your calculations in part 1 of the Data and Questions section below.

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<u>Part 2</u>: pH of Salt Solutions

1. For the six salt solutions in the Data Sheet, estimate the pH as acidic, neutral, or basic. Record your predictions before proceeding to #2!

2. Once your predictions are complete, read the pH meters immersed in the salt solutions and record the actual pH values on your data sheet. How closely do your predictions correlate with the actual experimental results? Make corrections if needed. Write the molecular equation, complete ionic equation, and net ionic equation for each of the salt solutions in the Data Sheet.

<u>Part 3</u>: Determination of K_a of an Unknown Weak Acid and Properties of a Buffer

1. Obtain a solid sample of an unknown acid. Dissolve approximately 1 g of the unknown sample in 50 mL D.I. water in a 250-mL Erlenmeyer flask. Pour all of the solution into a graduated cylinder read the volume and pour back half of the volume into the original Erlenmeyer flask. Save the other half in the graduated cylinder for step 3 below.

2. Add 2 drops of phenolphthalein indicator into the Erlenmeyer flask and titrate it with the standardized NaOH solution. Volume readings need not be taken here. As the endpoint approaches, add the titrant drop by drop until the solution has a permanent pale pink color.

3. Add the other half of the solution that you set aside (in a graduated cylinder) into the titrated solution in the Erlenmeyer flask. Swirl the solution well. ***This solution is now HALF-NEUTRALIZED.***

4. Rinse the pH meter well over a beaker with D.I. water each time you will measure a new pH value. NEVER wipe the electrode with a paper towel; this can damage the probe. Now measure the pH of the half-neutralized solution using the pH meter. From the observed pH, calculate the K_a of your unknown weak acid using the space provided in part 3 of the Data and Questions section below.

5. The half-neutralized solution is a buffer. Place 20 mL of this buffer in a 100 mL beaker. Measure the initial pH of this 20 mL buffer transferred to a clean 100 ml beaker, add 5 drops of 0.1 M HCl and mix thoroughly. Measure the pH of the resulting solution. Place 20 mL of tap water in another clean 100 mL beaker. Measure the initial pH of this 20 mL tap water in another clean 100 mL beaker. Add 5 drops of 0.1 M HCl into the tap water, mix thoroughly and measure the pH of this acidic solution.

6. Repeat step 5 above, this time adding 0.1 M NaOH (instead of 0.1 M HCl) into a clean beaker containing a new sample of 20 mL of the buffer (half neutralized solution) and a new sample of 20 mL tap water.

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Part 4: Determination of the Equivalent Mass of an Unknown Acid

1. Accurately weigh a sample of your solid unknown acid (the appropriate mass is written on the unknown container). *Make sure to record the unknown number and mass*.
2. Dissolve the sample in 30 mL D.I. water and titrate it to the phenolphthalein end point.
3. Repeat one more time. Choose a mass for the second sample so that the volume of NaOH needed will be about 15 mL.
4. Calculate the gram equivalent mass of your sample.

Part 5: Determination of the GEM and K_a of an Unknown Acid from a Titration Curve

1. In a 150 ml beaker, weigh and record a sample of your acid that requires about 15 mL of base to reach the equivalence point. *[(acid mass/base volume)$_{part\ 4}$ x15]*
2. Dissolve the sample in approximately 50 mL D.I. water.
3. Set up the computerized LabQuest Mini drop counter and pH meter to construct a weak acid/strong base titration curve. Rinse the pH meter well with D.I. water. NEVER wipe the electrode with a paper towel; this can damage the probe. The magnetic stirrer is attached to the pH probe.
4. Check and set the drop calibration to the correct number of drops per mL: Click on experiment/calibrate/drops per ml and change if necessary to match the drops stated on the dropper instrument containing the standardized NaOH. Verify that the volume of NaOH in the dropper is sufficient.
5. Place your 150 mL beaker on a magnetic stirrer. Insert the pH electrode so it is submerged in your acid solution, you may need to add more water. Turn on the magnetic stirrer. Caution: DO NOT TURN ON HEAT. Line up the dropper so that each drop will pass through the infrared sensor and be measured. Set the experiment to collect. Slowly start drops falling and check to see if they are measured and recorded. Continue the titration curve until about 5 mL beyond the equivalence point. The LabQuest Mini will record the volume of base for each drop and pH of the solution during the titration.
6. Stop the collection and click on analyze/examine. Move the mouse curser to the equivalence point on the graph and record the volume and pH at equivalence. Similarly, record the half equivalence volume and the half-equivalence pH.
7. Save the graph by taking a picture or sending it to your email as an Excel® file or pdf.
8. From the graph, determine the pK_a of the acid, that is, the pH where the acid is half-neutralized. Calculate the K_a value of your acid.
9. Determine the volume of NaOH needed to reach the equivalence point from the graph and with your recorded mass of the acid used, determine the gram equivalent mass of your acid. Calculate the average of all three of the gram equivalent mass values from parts 4 and 5.

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Pre-Lab Questions: Buffers and Determination of Equivalent Mass and K_a of an Unknown Acid

1. What is the equivalent mass of each of the following acids?
    1. $HC_2H_3O_2$
    2. $KHCO_3$
    3. H_2SO_3
    4. H_3PO_4

2. It is found that 24.6 mL of 0.116 M NaOH is needed to titrate 0.293 g of an unknown acid to the phenolphthalein end point. Calculate the equivalent mass of the acid.

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Data and Questions

Part 1A: pH of Unknown and Buffer Solutions

Enter in the appropriate space the name of the indicator used, the observed color of unknown after addition of the indicator, and the estimated pH value from the pH paper for the unknown.

Liquid Unknown #: _________

pH paper estimate: ________________ (3-pH unit range)

Indicator Used	Color of Unknown	Color of Buffer pH = _______	Color of Buffer pH = _______	Color of Buffer pH = _______

Estimate pH based on matching of colors = ___________ (within 0.5 pH unit)

Part 1B: pH of Acetic Acid Solutions

(Note: HAc = $HC_2H_3O_2$, acetic acid).

	1.0 M $HC_2H_3O_2$	0.10 M $HC_2H_3O_2$	0.010 M $HC_2H_3O_2$
pH			
K_a			
% dissociation			

SHOW YOUR CALCULATIONS ON THE NEXT PAGE.

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1.0 M $HC_2H_3O_2$ (aq):

0.10 M $HC_2H_3O_2$ (aq):

0.010 M $HC_2H_3O_2$ (aq):

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Part 2: pH of Salt Solutions

1. PREDICT whether each of the salt solutions below is expected to be acidic, neutral, or basic:

$NaCl$ __________ $NaC_2H_3O_2$ __________ Na_2CO_3 ____________

NH_4Cl _________ KNO_3 _____________ $ZnCl_2$ ______________

2. Using the pH meter immersed in each salt solution, determine the actual pH:

$NaCl$ __________ $NaC_2H_3O_2$ __________ Na_2CO_3 ____________

NH_4Cl _________ KNO_3 _____________ $ZnCl_2$ ______________

3. Write balanced MOLECULAR, IONIC, and NET-IONIC equations for the hydrolysis reactions of each salt solution. From the net-ionic equation, verify that the reaction is acidic, neutral or basic.

A. $NaCl(aq)$:

Molecular:

acidic neutral or basic?

Ionic:

_____ Net-Ionic:

B. $NaC_2H_3O_2(aq)$

Molecular:

Ionic:

_____ Net-Ionic:

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C. $Na_2CO_3(aq)$

Molecular:

Ionic:

_____ Net-Ionic:

D. $NH_4Cl(aq)$

Molecular:

Ionic:

_____ Net-Ionic:

E. $KNO_3(aq)$

Molecular:

Ionic:

_____ Net-Ionic:

F. $ZnCl_2(aq)$

Molecular:

Ionic:

_____ Net-Ionic:

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Part 3: Determination of K_a and Properties of a Buffer

Solid Unknown Number: ____________

1. Original pH of the half neutralized solution: ___________

2. Calculate K_a of the Weak acid:

3. Fill in table:

	tap water (original pH)	tap water (pH after)	Buffer (original pH)	Buffer (pH after)
addition of 0.1 M HCl				
addition of 0.1 M NaOH				

4. How does the table above show that the half-neutralized solution is indeed a buffer?

5. Using the data on your table above, comment on the buffering ability of your half-neutralized solution in comparison to the tap water.

6. Comment on the comparison between adding a strong acid vs a strong base to your buffer solution (i.e. is this solution more resistant to an increase or a decrease in pH?).

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Part 4: Determination of the Equivalent Mass of an Unknown Acid

Given: __________ M NaOH

Fill in the table below

Sample	Mass unknown acid (g)	Volume NaOH used (mL)	Volume NaOH used (L)	Mol NaOH equal to Mol H^+	Gram Equivalent Mass of Acid (g/mol H^+)
Trial 1					
Trial 2					
					Average GEM: _________ g/mol H^+

Show sample calculations below

Part 5: Determination of the K_a and Equivalent Mass of an Unknown Acid using LabQuest Mini

Use the same unknown sample as part 4. Solid Unknown Number: _______

1. Determine the approximate mass desired to reach the equivalence point in approximately 15 ml of NaOH added.

   Approximate mass to use = (mass of acid/volume of base)$_{part\ 4}$ x 15ml desired

2. Mass accurately weighed into a clean, dry 150 ml beaker. ____________

3. Using the graph, determine the volume and pH of titrant at equivalence point.

   Volume ______________ pH ___________

4. Using the graph, determine the volume and pH at the half-equivalence point.

   Volume ______________ pH ___________

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5. Solve for the pK_a, K_a, and gram equivalent mass of your unknown acid using the data collected in part 5.

   Unknown #: _______

6. Calculate the average of all three GEM that you determined (two from part 4 and one from part 5).

7. Why is the equivalence point NOT at pH 7?

8. Identify the following areas on the weak acid/strong base titration curve.
   A) Weak acid
   B) Buffer zone
   C) Equivalence point, salt
   D) Strong base zone
   E) Half equivalence point

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Post-Lab Questions: Buffers and Determination of Equivalent Mass and K_a of an Unknown Acid

1. A buffer was prepared by mixing 50.0 mL of 0.10 M HX and 25.0 mL of 0.10 M NaOH. The K_a of HX is 1.5×10^{-6}. Calculate the pH of this buffer.

2. The following values were experimentally determined for the titration of 0.145 g of a weak acid with 0.100 M NaOH:

Volume of NaOH, mL	**pH**
0.0	2.88
5.0	4.15
10.0	4.58
12.5	4.76
15.0	4.93
20.0	5.36
24.0	6.14
24.9	7.15
25.0	8.73
26.0	11.29
30.0	11.96

A. Construct a titration curve (pH vs Volume of NaOH).

B. Examine the graph for the required volume to reach the equivalence point?

C. Examine the graph and state the pH at the half-equivalence point?

D. Determine the K_a of the acid.

E. Calculate the gram equivalent mass of the acid.

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3. The following acid-base indicators are available to indicate the end point of this weak acid/strong base titration. Which of them would be most appropriate? Explain.

Indicator	**Color Change**		**pH Transition**
	Acid Form	**Base Form**	
Bromphenol blue	yellow	blue	3.0-5.0
Bromthymol	blue	blue	6.0-7.6
Thymol blue	yellow	blue	8.0-9.6