K_a Acid Dissociation Constant

Minneapolis Community and Technical College
Principles of Chemistry II, C1152
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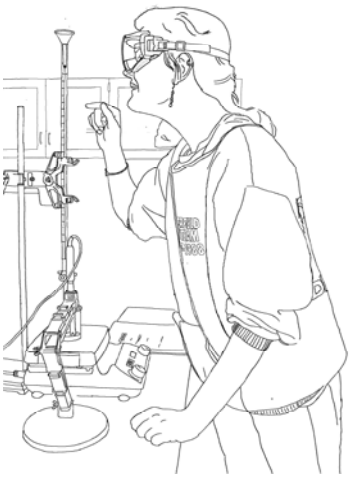


I. Introduction

Monoprotic acetic acid, $CH_3COO\mathbf{H}$ is sometimes written as $\mathbf{H}CH_3COO$, $\mathbf{H}C_2H_3O_2$ or even **H**A to acknowledge the *one* ionizable hydrogen, attached to an oxygen atom that is responsible for the acid's characteristic acid behavior. The three hydrogen atoms attached to the carbon atom are strongly bonded and thus don't contribute significantly to acidic behavior.

Acetic acid is also a *weak* acid. When pure glacial acetic acid (containing no water) is dissolved in water, some acetic acid molecules react (the *forward* reaction) with water to form hydronium and acetate ions:

$$CH_3COO\mathbf{H}_{(aq)} + H_2O_{(l)} \quad < \text{---} > \quad H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

Acetic Acid ***Hydronium*** ***Acetate***

Simultaneously, acetate and hydronium ions *recombine* to form the original products (the *reverse* reaction). This equilibrium situation leaves most of the acetic acid molecules in their molecular form and only few as acetate ions. Thus, the solution contains relatively few ions and is a weak electrolyte and thus a weak conductor of electricity.

The equilibrium constant for the reaction above, K_a, depends on the concentrations of product and reactant species as follows:

$$K_a = \frac{[H_3O^+] \times [CH_3COO^-]}{[CH_3COOH]} \qquad \textbf{Equation 1}$$

It will be the goal of this experiment to calculate the value of K_a in a variety of different situations and to compare it to the known value of 1.76×10^{-5} at 25°C. The calculation will require mole and total volume information for all species used to calculate concentrations and lastly K_a.

Calculation of K_a for a weak acid *(Experimental solutions #1 and #2)*

To calculate K_a, the equilibrium concentrations of H_3O^+, CH_3COO^- and CH_3COOH must be known and substituted into the formula above (Equation 1).

1. **$[H_3O^+]_{eq}$** is determined by first measuring the pH of the solution with the pH meter. The pH reading is then used to calculate $[H_3O^+]$:

$$[H_3O^+]_{eq} = 10^{-pH} \qquad \textbf{Equation 2}$$

2. **$[CH_3COO^-]_{eq}$** : From the balanced chemical equation, we see that $moles_{CH_3COO^-} = moles_{H3O+}$ Therefore,

$$[CH_3COO^-]_{eq} = [H_3O^+]_{eq} \qquad \textbf{Equation 3}$$

3. **$[CH_3COOH]_{eq}$** Because CH_3COO^- and H_3O^+ are produced at the expense of consumed CH_3COOH in a 1:1:1 mole ratio, the new concentration of CH_3COOH can be easily calculated:

$$[CH_3COOH]_{eq} = [CH_3COOH]_{initial} - [H_3O^+]_{eq} \qquad \textbf{Equation 4}$$

…where $[CH_3COOH]_{initial}$ refers to the un-dissociated acid concentration before equilibrium is achieved. For weak acid solutions, this value is the concentration specified on the bottle label.

4. K_a determination. Substitute the values obtained from steps 2, 3 and 4 into Equation 1 above.

Buffer Solutions *(Experimental solutions #3 and #4)*

Buffers are solutions of a weak acid and its conjugate base. Such solutions are used to maintain pH at constant levels. Determining the pH of a buffer solution is very similar to determining the pH for the weak acid solution above except that the initial concentration of base (CH_3COO^-) is NOT initially zero.

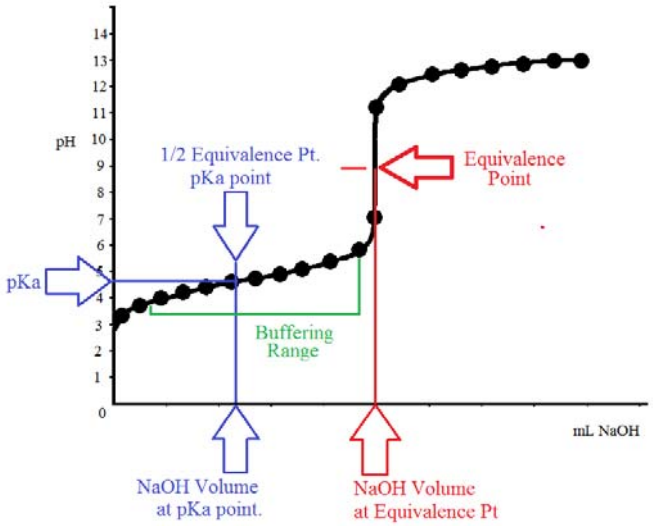
For example, a buffer could be constructed from 50.0 mL of 1.0 M CH_3COOH mixed with 100.0 mL of a 1.0 M **$NaCH_3COO$** solution. The latter contributes **CH_3COO^-** (conjugate base) along with the **Na^+** spectator ion. Once mixed, their respective ***initial* concentrations** can be determined via dilution calculations (you should confirm this):

	$CH_3COOH_{(aq)}$	+	$H_2O_{(l)}$	< --- >	$H_3O^+_{(aq)}$	+	$CH_3COO^-_{(aq)}$
Initial	**0.3333 M**		~		**0.00M**		* **0.6667 M**
Change	***-x***		~		***+x***		***+x***
Equilibrium	**0.3333 M - *x***		~		***+x***		* **0.6667 M + *x***

Once a pH value for the combined solutions is measured, a value for $[H_3O^+]$ is determined. This value is used to calculate the new equilibrium concentrations of the other species. Note that unlike a pure weak acid solution, the initial concentration of the conjugate base is NOT initially zero. Consequently, its equilibrium level is determined by adding "x" to the initial concentration (* above). Finally, K_a is determined by substituting the equilibrium concentrations into equation 1 above.

pH titration curves (Titration of CH_3COOH)

A graph of pH (Y) vs mL (X) is known as a titration curve. You will construct such a graph by titrating a weak acid incrementally with the strong base NaOH. After each 0.4 mL addition of NaOH you will measure the pH of the solution until the pH has reached a high level. The graph of your results will resemble the figure at right.



1. **Equivalence point:** the point in the titration where the acid and base are just neutralized often identified by a color change associated by an indicator. Because NaOH and CH_3COOH react in a 1:1 mole ratio, the equivalence point occurs when the number of moles of acetic acid equals the moles of NaOH.

The slope of the graph in the vicinity of the equivalence point is very steep. Consequently, it is unlikely you will have more than one or two points on the line. However, the equivalence point can still be identified as ½ way up the slope. This may require a ruler and probably won't coincide with one of your data points.

Note that when titrating a strong acid with a strong base, the equivalence point occurs at pH=7. However, this is not the case when titrating a weak acid with a strong base as we are in these experiments.

2. **½ equivalence point**: This point, also known as the **pK_a point**, is where the moles of added base are equal to half the moles of acid originally present. This point is identified by locating a point ½ through the horizontal section of the graph (see buffering region below).

The pK_a value is determined by drawing a horizontal line from the ½ equivalence point to where it intersects the "pH" axis. This value can then be used to determine a value for K_a via the following formula:

$$K_a = 10^{-pKa} \qquad \textbf{Equation 5}$$

3. **Buffering range**: This is the range over which the solution maintains an approximately constant pH. The buffering range is identified by first locating the pK_a point (above). The pH limits of the buffering range are pK_a +1 and pK_a -1. Thus, if the pK_a value was 3.5, the buffering range limits would be pH = 2.5 and pH = 4.5.

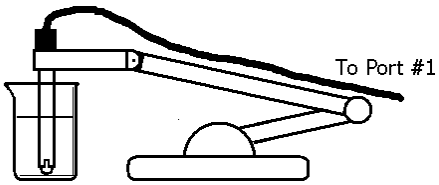
Note that although the pH is approximately constant throughout the buffering range, it does increase slowly as the buffering action is not perfect. Once we near the equivalence point, the pH changes dramatically as the buffer is exhausted.

pH Probe Operation

The pH probe you'll be using in this experiment is a delicate electrochemical cell that generates an electrical voltage when immersed in aqueous acidic or basic solutions. This voltage is measured and then converted into a pH value by the computer before being displayed as pH.

Before use, the pH probe must be removed from its storage solution (left). Carefully loosen the cap several turns and pull the pH probe free from the vial. Put the vial and lid in a safe place where it won't be knocked over and spilled. You'll return the pH probe to the storage vial when finished with your measurements.

Now insert the pH probe into the articulated arm (right) and immerse the bottom of the probe in a small beaker of distilled water. When not performing measurements, the pH probe should be returned to the distilled water to keep it from drying out.



Between uses, the pH probe should be rinsed with distilled water from a squirt bottle. Have a spare beaker handy to catch the rinse solution. Also, gently blot or dab the end of the pH probe with a tissue or KimWipe to remove excess water. Be very careful as the end of the probe is made of glass that is easily broken (left).Also, <u>don't</u> scrub the probe to remove excess water.

The pH probes will not measure accurately without first being calibrated and you'll calibrate the probe once using two buffer solutions of known pH (2 & 12). Expensive, research grade pH probes and controllers automatically adjust the pH reading for changes in temperature but the probes you are using do not have this ability. Furthermore, these pH probes do "drift" a little. To minimize the drifting, be sure to stir or swirl the solution at all times to keep a flow of fresh solution in contact with the pH probe.

If you ever doubt the accuracy of your pH readings, you can check the calibration of the pH probe by re-measuring the pH values of the pH 2 and pH 12 buffer solutions. If these readings are significantly off, you will want to recalibrate the probe.

When you are finished with the pH probe, rinse it a last time and blot the end with a tissue. Carefully slide the lid from the storage solution vial onto the probe. <u>Position the lid properly so that the probe doesn't crash into the bottom of the storage solution vial as this will break the pH probe.</u> Insert the probe into the vial and make sure the probe doesn't touch the bottom as you screw on the lid.

At the end of the day, the pH probe should be left in a vertical orientation to keep the storage solution from leaking out. Your ring stand/burette clamp is a good place to hang the probe vertically for the next class.

II. PRELAB EXERCISE

Clearly answer these questions in INK in your lab notebook before coming to lab.

1. The pH = 3.75 for a 0.350 M weak acid (HA) solution.
   Determine $[HA]_{eq}$, $[H_3O^+]_{eq}$, $[A^-]_{eq}$ and K_a for this acid.

2. How is a buffer different from its corresponding weak acid solution?

3. List three precautions you should be aware of when using a pH probe.

4. In an acid/base titration, the equivalence point is reached when 22.56 mL of NaOH is added.
   How many mL are required to reach the pK_a point in the same titration?

III. Word Processed Report

Page 1: *Upper right hand corner Name, Lab section number and date*

Titration Graph: Clearly identify the buffering range, pK_a point and equivalence point.

Page 2 &3: ***Complete I.C.E. problem solution for the first four solutions.***

For each solution include these details:

- *Measured pH*
- *pH to H_3O^+ calculations*
- *Dilution calculations (Solutions 2, 3 & 4)*
- *Balanced chemical equation*
- *Initial, Change and Equilibrium entries (beneath the equation)*
- *Any important "math"*
- *Calculated value of K_a with the correct number of significant figures.*
- *Δ% (use 1.76 × 10^{-5}* as the known value)

Δ% is a value that tells us relatively how our experimental value compares to the known value and whether the experimental value is high or low. Calculate the Δ% as follows and don't forget to report the sign (+/-) in your result.

$$\Delta\% = \frac{(Experimental - Known)}{Known} \times 100$$

Page 4 Answers to the following questions:

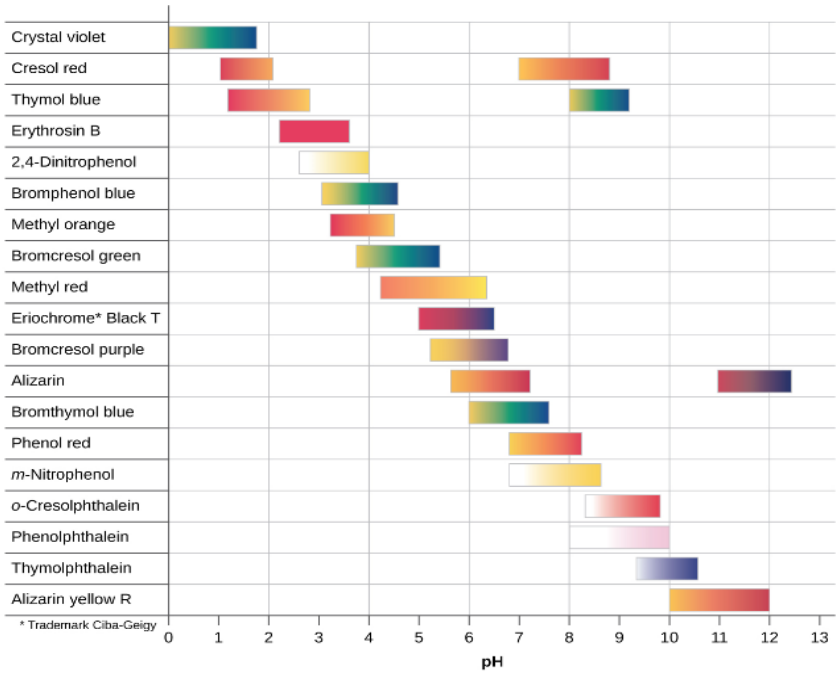
1. Identify an appropriate indicator for the CH_3COOH/NaOH titration from the table below. What color change would you expect to see at the equivalence point using this indicator?

(Obtained from: http://cnx.org/resources/07513b9f959376242382da61f18f5e2bf8d58fe4/CNX_Chem_14_07_indicators.jpg)

2. If methyl orange had been used as an indicator in today's titration, would the color change correctly identify the equivalence point of the titration? Why? Why not?

3. Determine the volume of NaOH used to reach the equivalence point in your titration. Include this labeled value on your graph. Calculate the number of moles of NaOH that have been added and compare this value to the number of moles of CH_3COOH that were originally present. They should be equal. Are they? (Show your calculations)

4. Calculate K_a and Δ% using the pK_a value you obtained from your graph. ($K_a = 10^{-pK_a}$)



IV. Procedure

A. Solution Preparation

…You will be working in pairs today.

** Download and print the handouts re. burette, volumetric flask, and volumetric pipette techniques available on the chemistry web site.*

Prepare each of the following 4 solutions using the stock 1.00 molar acetic acid stock solution provided in the laboratory.

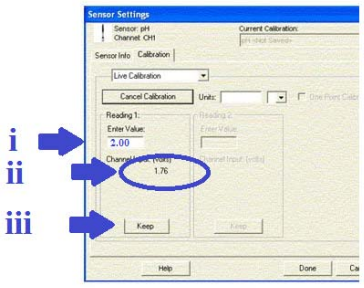
- **Solution #1**
  - Dispense approximately 50 mL of 1.00 CH_3COOH solution in a clean/dry 100mL beaker
- **Solution #2**
  - Obtain a 100 mL volumetric flask
  - Pipette 10.00 mL 1.00 M CH_3COOH into the volumetric flask.
  - Add distilled water to the volumetric flask up to the line. Use a wash bottle or eyedropper for the final additions.
  - Stopper and mix thoroughly
- **Solution #3: Buffer Solution A**
  - Use the supplied graduated cylinders to dispense 100.0 mL 1.00 M $NaCH_3COO$ (sodium acetate) and 40.0 mL of 1.00 M CH_3COOH in a clean/dry 250 mL beaker.
  - Mix well using a clean glass stirring rod.
- **Solution #4: Buffer Solution B**
  - Take 10.00 mL of solution #3 and dilute with 90.0 mL of distilled water in a 150mL beaker.

B. pH probe calibration

Note: Whilst calibrating the pH probe, the large screen pH display is locked and won't change.

1. Remove the pH probe from the storage solution by unscrewing the cap.
2. Insert the pH probe in the buffer vial and stir the solution by moving the pH probe with an up and down motion.
3. Click on…
   a. "Experiment"
   b. "Calibrate" and then pH probe (menu pops up to right of calibrate menu)
   c. Click on "Calibrate Now"
   d. Enter the buffer's pH value in the field next to "Enter Value" (either 2 or 12) …see "i" in picture below

8. Continue stirring with an up and down motion. When the voltage associated with "input 1" (ii) stabilizes click "Keep"



9. Rinse the pH probe with distilled water and blot dry with a tissue.
10. Immerse the pH probe in the second buffer's vial and stir with an up and down motion.
11. Enter the second buffer's pH value in the field next to the "value 2" in the calibration menu.
12. Continue to swirl the beaker and when the voltage next to "input 2"
13. When the input 2 voltage stabilizes, click "Keep"
14. Click "Done"
15. Check your pH probe's calibration by measuring the pH's of the 2 and 12 buffer. Recalibrate if necessary.
16. Don't shut down Logger Pro until you are finished making pH measurements as the calibration will be lost.

C. pH measurement

1. Pour approximately 20 mL of the solution to be tested into a clean, dry 50 mL beaker.
2. Immerse the pH probe in the solution and swirl the solution.
3. **Swirl the solution constantly** and record the pH reading in your notebook.
4. Rinse the beaker with a few mL of the next solution and dispose of the rinse solution.
5. Measure/record the pH. Repeat the procedure for the remaining solutions.
6. Discard all solutions in the sink EXCEPT solution #1. You will use this solution in part D.

D. Titration of a weak acid

1. Place 15.0 mL of solution #1 in a 100 mL beaker
2. Add an additional 15.0 mL of distilled water and stir.
3. Add a magnetic stir rod and place the beaker on an unheated stir plate
4. Begin stirring (~300)
5. Position the pH probe in the solution using the articulated arm
6. Rinse and fill a buret with 1.0 M NaOH solution.
7. Position the buret over the stirred beaker.
8. Add the NaOH in 0.4 mL increments. Wait ~5 seconds before recording the burette reading and the pH for each addition.
9. Continue adding base until the pH has leveled off at high pH (pH ~12).
10. Dispose of all solutions in the sink