Identification of a Weak Acid by Titrimetry

adapted from Bell,Richard and Crook, J.R., Identifying a Weak Acid by Titrimetry, Chemical Education Resources, 2000.

Goals and Challenges:

The goal of this experiment is to use computer-based pH measurements to prepare a titration curve for the titration of an unknown weak acid with sodium hydroxide solution (NaOH). A plot of the first derivative of the titration curve will be graphed and used to determine the volume of NaOH needed to reach the titration equivalence point. The pK_a and equivalent mass of the unknown acid will be calculated and will be used to identify the unknown acid from a list of possible unknown weak acids.

Bring to lab: • **Lab notebook** • **Safety eyewear, lab coat, closed-toe shoes, long pants**	**Suggested Reading:** • **Section 14.7 Acid-Base Titrations (particularly titration of a weak acid with a strong base) in the OpenStax text*** **Pre-lab work (in your lab notebook):** • **Short summary of the experiment** • **Written pre-lab assignment (see below)** • **Procedural outline to be followed during lab, including Data Tables 1 and 2**

* OpenStax provides an open source online Chemistry textbook that can be found at https://openstax.org/details/books/chemistry-2e. You can choose to view the textbook online, or download a PDF.

Pre-lab Assignment

This lab has prelab quiz (two tries) which you can find on the myCourses page. Read through all the background information first, and then answer the prelab questions.

Background Information:

Two distinguishing characteristics of an acid are its molar mass and its acid strength (identified by its K_a), both of which will be used to identify an unknown acid in this lab. The acid strength is measured by the extent to which the acid transfers H^+ to a base, which is usually water. The following equation and equilibrium expression for the proton transfer from an acid to water are shown below:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad \text{(Eq. 1)}$$

The equilibrium constant expression for the reaction in Equation 1 is shown in Equation 2:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \text{(Eq. 2)}$$

The greater the extent to which the acid transfers H^+ to water, the greater the acid strength of HA, and the larger the value of the acid dissociation constant, K_a. For example, HCl is a strong acid in water and transfers virtually all of its H^+ to water. The K_a of HCl is very large, approximately 10^8. By contrast, acetic acid ($HC_2H_3O_2$) and mandelic acid ($HC_8H_7O_3$) are weak acids that transfer only a fraction of their H^+ to water. The K_a of $HC_2H_3O_2$ is only 1.8×10^{-5}, and that of $HC_8H_7O_3$ is 3.89×10^{-4}.

For convenience, in comparing the strengths of weak acids, the K_a values are often expressed as pK_a values, as defined in Equation 3. The pK_a values of $HC_2H_3O_2$ and $HC_8H_7O_3$ are 4.74 and 3.41, respectively. Note that the weaker acid has the larger pK_a value.

$$pK_a = -\log K_a \qquad \text{(Eq. 3)}$$

Table 1 shows the molar mass and pK_a values for a number of monoprotic weak acids:

Table 1 *Molar masses and pK_a values for some weak acids*

Acid Name	*Chemical Formula*	*Molar Mass (g/mol)*	*pK_a*
acetic	$HC_2H_3O_2$	60.0	4.74
benzoic	$HC_7H_5O_2$	122.0	4.19
butyric	$HC_4H_8O_2$	88.1	4.83
chloroacetic	$HC_2H_2ClO_2$	94.5	2.85
trans-crotonic	$H_6C_4O_2$	86.1	4.69
mandelic	$HC_8H_7O_3$	152.2	3.41
potassium hydrogen phthalate	$KHC_8H_4O_4$	204.2	5.51
sodium hydrogen sulfite	$NaHSO_3$	104.1	7.21
sodium hydrogen tartrate	$NaHC_4H_4O_6$	172.0	4.34

Identifying an Unknown Acid

In this experiment, you will identify an unknown weak acid by titrating a sample of the acid with NaOH solution using the Vernier data acquisition system to record the pH as a function of volume added. From the titration data, you will determine the pK_a and equivalent mass of the unknown acid. You will then identify the acid by comparing your results with the data in Table 1. The procedure that you will follow is outlined below.

You will mass an amount of unknown acid and prepare a titration curve for the titration with standardized NaOH solution. Figure 1 shows a titration curve for the titration of an unknown acid with 0.0500 M NaOH.

Example 1: A student obtained the following titration curve by dissolving the acid sample in water and measuring the pH as increments of NaOH solution were added. Each addition of NaOH neutralized some of the acid, as shown in Equation 4. As the acid was neutralized, the H_3O^+ ion concentration decreased, and the solution pH increased.

$$HA + OH^-(aq) \rightleftharpoons A^-(aq) + HOH \qquad \text{(Eq. 4)}$$

Of greatest interest is the **equivalence point** of the titration, the point at which the number of moles of $OH^-(aq)$ added to the sample exactly equals the number of moles of HA(aq) present in the original sample. The equivalence point occurs at the steepest point in the titration curve.

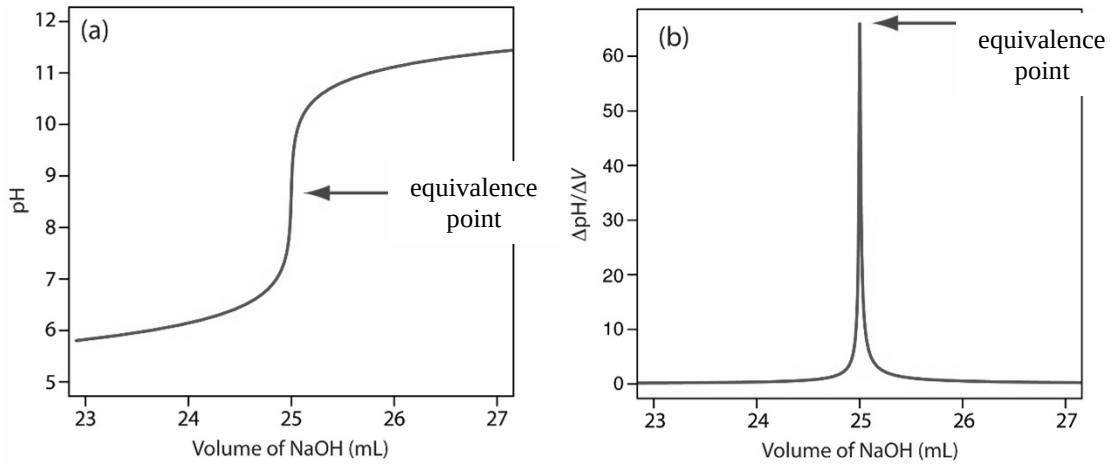


Figure 1. (a) Titration curve for the titration of an unknown acid with 0.0500 M NaOH. **(b)** First derivative of the titration curve shown in (a).

The student used the first derivative of the titration curve data in Figure 1a to determine the equivalence point accurately. To prepare the **first derivative curve**, the student first determined the titration curve slope at each of the experimental points. These slopes are the first derivatives of the pH values with respect to the NaOH volume added and are labeled Δ(pH)/ ΔV (or d(pH)/dV). A plot of Δ(pH)/ ΔV on the *y*-axis and the volumes of NaOH on the *x*-axis gave the first derivative curve, shown in Figure 1b. Note that the slope of the titration curve increases and decreases sharply in the vicinity of the equivalence point. The point at which the slope is at a maximum is the equivalence point, and the corresponding NaOH volume is the equivalence-point volume.

You can estimate the pK_a of the acid using any of the pH-volume data points from the titration. However, at one point in the titration, the determination of pK_a is especially straightforward. When **one-half** of the acid has been titrated, **half of the acid has been converted to A^- (aq)**, and the other half is still HA (aq). This is the ***half-equivalence point***. At this point, $[A^-] = [HA]$, and we can simplify Equation 2 to the expressions in Equation 4 and Equation 5.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \text{(Eq. 2)}$$

At the half-equivalence point,

$$K_a = [H_3O^+] \qquad \text{(Eq. 4)}$$

$$pK_a = pH \qquad \text{(Eq. 5)}$$

Note that Equations 4 and 5 are valid ***only*** at the half-equivalence point.

To determine the equivalent mass of the unknown acid, you will first use Equation 6 to calculate the number of moles of NaOH required to titrate the acid to the equivalence point.

$$\text{(number of moles NaOH)} = \text{(molarity, mol/L)(volume, L)} \qquad \text{(Eq. 6)}$$

The number of moles of NaOH required to reach the equivalence point equals the number of moles of unknown acid originally present in the sample. You will calculate the molar mass of the acid by dividing the mass of the sample by the corresponding number of moles, as shown in Equation 7:

$$\text{molar mass, g/mol} = \frac{\text{mass of unknown acid, g}}{\text{number of moles of unknown acid}} \qquad \text{(Eq. 7)}$$

Example 2: **Sample Calculation**

A student obtained the titration curve similar to the one shown in Figure 1 by dissolving a 0.1527-g sample of unknown acid sample in 50 mL of water and titrating it with 0.0500 M NaOH. From the first derivative curve similar to the one shown in Figure 1, the student determined the equivalence-point volume to be 24.96 mL of NaOH solution.

The half-equivalence point occurs at (1/2)(24.96 mL) = 12.48 mL NaOH. The pH at the half equivalence point is 4.25 (this is determined from the graph of the titration curve; the graph in Figure 1 is too far zoomed in to show this point), and therefore the pK_a of the unknown acid is 4.25.

Referring to Table 1, the most likely identity of the acid is benzoic acid (pK_a = 4.19) or sodium hydrogen tartrate (pK_a = 4.34). These two acids have very different molar masses, and the student was able to identify the unknown acid with confidence from its molar mass.

Using Equation 6, the number of moles of NaOH = (0.0500 M)(0.02496 L) = 1.248×10^{-3} mol. which is equal to the number of moles of acid in the original sample. Hence, using Equation 7, the molar mass is 0.1527 g/(1.248×10^{-3} mol) = 122 g/mol.

From the calculated pK_a (4.25) and molar mass (122 g/mol), the student concluded that the unknown acid is benzoic acid (see Table 1).

THE INVESTIGATION

Overview

You will work in **groups of two** for this lab so that each of you has hands-on experience with titrating. You will perform several titrations, some of which will be done manually (Part I) and one with the computer interface (Part II). The manual titration with an indicator can accurately provide information on the endpoint of the titration and is quick, but provides little other information. The volume of NaOH used to reach the endpoint is all that is needed in Part I. However, the full titration curve (pH vs. volume added) is needed for Part II and you will collect and plot the volume and pH data using **LoggerPro**.

Glassware: For this experiment, you will be provided with any glassware and equipment not found in the drawer at your bench. You will use one large beaker, one 250 mL beaker, one 150 mL beaker, 2 125 mL Erlenmeyer flasks, and graduated cylinders from the drawer at your bench. A buret will be set up at your station. Extra 125 mL Erlenmeyer flasks (1 per group) will be provided on the front bench.

Part I: Preparing a Standardized NaOH solution

A. Preparation of NaOH base solution (≈ 0.05 M NaOH)

Using deionized water, prepare 300 mL of approximately 0.05 M sodium hydroxide in a 400 mL beaker by diluting the 2 M NaOH solution located in the fume hood. For various reasons, the solution you have prepared will not be exactly 0.05 M. It is, however, necessary that you know what its molarity is as accurately as you are able to determine it. The most accurate method which you have available is to **standardize** it by titrating a standard acid of known composition or molarity with your sodium hydroxide solution. The standard acid you will be using is **potassium hydrogen phthalate, $KHC_8H_4O_4$**. Since the number of moles of acid is equal to the number of moles of base at the titration endpoint, you will be able to calculate the number of moles of base and, with the volume of base used, molarity of the base solution very precisely.

- Calculate the amount of 2 M NaOH needed to prepare 300 mL of 0.05 M NaOH. *This should have been done as part of your pre-lab assignment. If you are unsure, ask your TA to confirm your calculated volume of the stock solution.*

Note: While one person prepares the base solution, the other partner can weigh out the potassium hydrogen phthalate (KHP) as instructed below.

B. Standardization of NaOH solution

1. Label three weigh boats or weighing papers "KHP". Weigh approximately 0.300 g of potassium hydrogen phthalate, KHP, to the nearest 0.001 g, on an analytical balance. Record the mass of KHP displayed on the scale (to the milligram). Weigh a second and third sample of KHP in the same manner and try to keep each mass within 10 mg of the first mass.

2. Clean three 125 mL Erlenmeyer flasks. Label the flasks for each sample (1, 2, and 3). Dissolve each KHP sample in about 70 mL of deionized water.

3. Place a short-stem funnel in the buret. Rinse the buret two or three times with ~5 mL portions of the NaOH solution, and drain thoroughly each time, discarding the solution into a large beaker (400 – 1000 mL size, in the drawer at your lab bench) labeled "Waste." Fill the buret to a point above the graduated scale, place the "Waste" beaker under the buret, and open the stopcock to fill the tip and force out all of the air. Tap the sides of the buret to dislodge any air bubbles. Make sure the tip is filled with liquid. Drain out the solution until the meniscus is on the first graduation at 0.00 mL (or another easy-to-read graduation near 0). Record this value as the initial buret reading for sample 1 in Data Table 1 in your lab notebook.

4. Add 4 drops of phenolphthalein indicator to the KHP solutions to help you visually see the progress of your titration.

5. Tilt the first flask of KHP to one side and slide a magnetic stir bar into it. Place the flask on a stir plate and adjust the stir speed. Titrate with the NaOH solution to the appearance of the **first** faint pink color that persists for longer than 30 seconds (approximately 30 mL titrant). Record the final buret reading in Data Table 1 in your lab notebook.

6. Repeat the titration twice more, recording the initial and final buret readings each time in Data Table 1 in your lab notebook. If one of your volumes is inconsistent, run another titration and remove the outlier. You should expect no more than 1 to 2 mL difference between titrations, depending on how close in mass you kept your KHP samples. Calculate the molarity of the NaOH solution to the proper number of significant figures and record in Data Table 1 in your lab notebook. (Molar mass of KHP = 204.23 g/mol)

- Determine the molarity of the NaOH titrant for each titration to three significant figures and average the values. Show your work. Record all values in Data Table 1 in your lab notebook.
- Once you have made this measurement, be sure to only use this sample of NaOH for the rest of the experiment. If you run out of the NaOH solution and have to make more by diluting the stock solution again, you will need to repeat the standardization.

Part II: Titrating the Unknown Acid

Caution: *The unknown acids and 0.05M NaOH are toxic and corrosive.*

Note: *pH sensors are expensive (~$100 each). The glass bulb at the tip is fragile. Do not knock the bulb, and handle the sensor carefully. Inform your TA if the probe does not calibrate or pH fluctuates and does not settle down to a consistent reading in a solution.*

A: Calibration of Vernier pH sensor

1. Connect the pH sensor to the LabQuest unit (Channel 1-3).
2. Open Logger Pro and load the experiment file for the acid-base titration (**Chemistry with Vernier → 24a-Acid Base Titration**).
3. Select **Experiment → Calibrate → pH sensor**. Click on **Calibrate Now.**

4. Move the probe from the pH 4-KCl storage solution to the pH 4 buffer solution. Wait **30** seconds, type 4.00 (Reading 1), and press **Keep.**
5. The cursor will move to the box for Reading 2. Rinse the sensor well with deionized water and place in the pH 7 buffer solution. Wait **30** seconds, type 7.00, and press **Keep.**
6. When calibration is complete, click **Done**.
7. Rinse and store the sensor in the pH 4-KCl storage bottle provided until ready to use. **The sensor should always be in the storage solution when not in use so that the glass bulb never dries out.**

Note: Once you have calibrated the pH sensor, make sure you do not unplug it from the controller or close the Logger Pro experiment file. If you open a new Logger Pro experiment, quit and restart Logger Pro, or disconnect and reconnect the pH sensor, you will lose the pH calibration and need to repeat this part.

B. Preparation of the sample

Note: *Unless your TA specifies otherwise, perform **two** titrations to find the pK_a and equivalent mass of your unknown acid.*

1. Obtain a sample of unknown acid from your TA and **record the Sample ID of the unknown acid** in Data Table 2 in your lab notebook.

2. Rinse a clean 150 mL beaker with three small portions of deionized water.

3. Weigh approximately 0.15 g of unknown acid to the nearest 0.001 g on an analytical balance. Record the mass of the unknown acid in Data Table 2 in your lab notebook.

4. Transfer the unknown sample carefully to your beaker and dissolve it in 50 mL of deionized water, measured using a graduated cylinder. Add 4 drops of phenolphthalein indicator to the solution. Place a stir bar carefully into the beaker and center the beaker on the stir plate. Place the calibrated pH probe in the beaker.

C. Titration with volume entry:

Read this before starting. *You are now ready to begin the titration. Initially, add NaOH in 1 mL increments. As you near the equivalence point (when pale pink begins to appear but disappears with stirring), reduce the increment size to obtain data points with pH values about 0.2 pH units apart. The more data points you obtain in this region, the more precise your equivalence-point determination will be. Beyond the equivalence point, you can again add larger increments of NaOH.*

1. Fill your buret to as close to 0.00 mL as you can. Record this value as the initial buret reading in Data Table 2 in your lab notebook. (See step 6 below – it is possible to correct for a non-zero starting volume, but easier if you do not have to).

2. In **Experiment → Data Collection → Mode**, choose **Events with Entry** on the pull-down menu and press **Done**. Press **Collect**; when the pH reading stabilizes, press **Keep** and record your starting volume (buret reading) at the prompt.

3. Add an increment of NaOH (you may start with ~1-2 mL). When the pH stabilizes, press **Keep** and then enter the buret reading (to the nearest 0.01 mL) at the prompt.

4. Repeat Step 7, adding smaller increments of NaOH (down to < 0.5 mL) when the pH begins to change significantly (as you near the equivalence point – the indicator will begin to turn pale pink). Continue to add increments of NaOH until the pH of the solution reaches **11** or **levels off**, whichever comes first. Press **Stop**.

Treating the Data:

5. Enter a calculated column (**Data Collection → New Calculated Column**) with a formula to adjust the NaOH volume values such that the starting volume is 0 (if the initial buret reading was greater than 0.00 mL, subtract the starting value from each volume value; this column is not needed if the initial buret reading was 0.00 mL for all titrations performed). Change the x-axis on the graph to the adjusted volume. (Double-click the graph to bring up the "Graph Options" dialog and select the new calculated column in the X-Axis box on the **Axes Options** tab).

6. First and 2nd derivative columns are automatically calculated and displayed in the columns labeled "d1" and "d2". The volume at the maximum of the first derivative is the equivalence point. The second derivative changes from positive to negative here as well.

7. Add the plot of the first derivative versus the volume of NaOH to same graph. Use the Right Y-Axis (also under Axes Options in the Graph Options dialog.).

- Calculate one-half the volume at the maximum first derivative. This is the volume when one half of the HA is dissociated to A^-.
- Look at the K_a equation. Simplify the K_a equation at this point. What do you notice?
- Use the graph to find the pH at this point. You can read it directly from the data column in LoggerPro if you happen to have collected a pH at that volume. If the half equivalence volume is between collected titration points, use **Analyze → Interpolate** and move the cursor to the correct volume to read the pH. Why is this point important?

8. Record the half-equivalence volume and pH on Data Table 2 in your lab notebook. You will need this information to identify your unknown.

9. Save a copy your graph to a blank Word file to include as part of your lab report.

10. **Repeat the titration and data analysis with a second solution of unknown acid** (unless instructed otherwise by your TA).

Part III. Shutting Down and Cleaning Up

1. After you finish your last titration, return the vial containing any unused unknown acid to your laboratory instructor.
2. Rinse the pH probe well with deionized water and store in the storage solution bottle. Return the buffer solutions to their original locations.
3. Pour any unused NaOH solution into your "Waste" beaker. Empty your "Waste" beaker and all titrated solutions into the labeled waste bottle in the fume hood.
4. Rinse the buret with 100 mL of water and drain contents in the sink. Turn the buret upside down and clamp in the buret holder.
5. Clean and return one 125 mL Erlenmeyer flask to the front bench.

6. Clean and put away all other glassware and equipment used in the experiment in the drawer at your bench. DO NOT leave any glassware, clean or otherwise, at any sink.

Caution: *Wash your hands thoroughly with soap before leaving the laboratory.*

These tables should be duplicated in your notebook. These tables will also need to be typed up and turned in with your report.

Data Table 1: Standardization of Base

Exact mass of KHP			
	Titration #		
	1	*2*	*3*
final buret reading, mL			
initial buret reading, mL			
volume of NaOH solution,mL			
calculated concentration of NaOH solution, M			
average molarity of NaOH, mol/L			

Data Table 2: Titrating the Unknown Acid **

Sample ID of unknown weak acid		
Concentration of NaOH solution (M)		
	Titration #	
	1	*2 (if done)*
mass of unknown acid,g (Use taring feature)		
initial buret reading (in mL)		
Final buret reading (in mL)		
Volume added (in mL)		
volume of NaOH solution required to reach equivalence point (in mL)		
volume of NaOH solution required to reach half-equivalence point (in mL)		
pH at half-equivalence point		
pK_a of unknown weak acid		
average pK_a of unknown weak acid		

** Remember to save a copy of your graph and include with your report.

Identification of a Weak Acid by Titrimetry

REPORT

Group Portion:

Part I. Preparing a Standardized NaOH solution.

1. Show the calculation for the preparation of 300 mL of 0.05 M NaOH from 2 M NaOH stock solution.

2. Submit a typed copy of Data Table 1, including the calculated and average NaOH concentrations.

3. Show your work or explain in words the calculation for one of the NaOH concentrations resulting from the titration.

Part II. Titrating the Unknown Acid

4. Submit a copy of your LoggerPro graph of the titration curve and 1st derivative of *pH* vs *mL NaOH*. You only need to submit one graph even if you completed both titrations.

5. Submit a typed copy of Data Table 2, complete with the equivalence point and half-equivalence point information you determined from the titration graph.

6. Use the equivalence-point volume and average NaOH concentration to determine the number of moles of NaOH required to reach the equivalence point and from that value, the number of moles of unknown acid titrated. Show your work for one of the calculations.

7. Calculate the molar mass of the unknown acid for each determination, and show your work for one of the calculations. Also give the average molar mass of the unknown acid (if replicates were done).

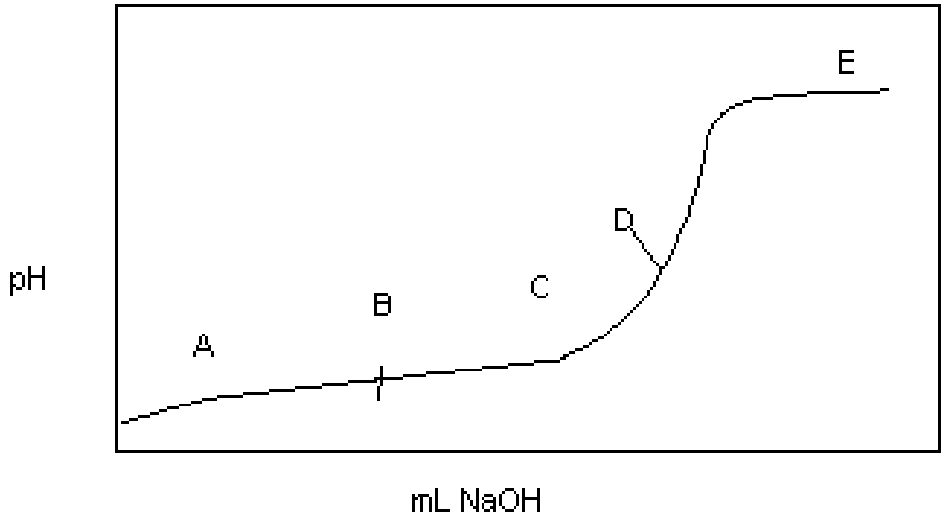
8. Record the name, pK_a, and molar mass of your unknown acid, and list the pK_a and molar mass of the acid from Table 1 that best matches the pK_a and molar mass that you obtained for your unknown.

	Experimental	Theoretical
a. pK_a	_____	_____
b. Molar mass	_____	_____
c. Name of acid	_____	

9. Assuming that you correctly identified your unknown acid, calculate the percentage error in your experimental determination the molar mass of the acid. (See Appendix A for the formula for percent error if you do not remember it).

10. What would be the pH at the half-equivalence point in titration of a monoprotic acid (HA) with NaOH solution if the acid has $K_a = 5.2\times10^{-6}$?

11. Compare the amount of undissociated acid (HA) to the dissociated acid (A^-), and compare the amount of H^+ to OH^- throughout the titration of a weak acid by a strong base described by the titration curve below (A: before the ½ equivalence point; B: at the ½ equivalence point; C: after the ½ equivalence point but before the equivalence point; D: at the equivalence point; E: after the equivalence point). (For region C, the relative concentrations of $[H^+]$ and $[OH^-]$ swap places. Explain which one starts greater and which one starts less).



Individual Portion:

1. Consider the titration of a weak base (B^-) with a strong acid (HCl). Draw (this can be hand drawn and scanned or sketched digitally) a pH (not pOH) vs mL HCl graph (it will not look the same as the one in question #13; if you start with a weak base, will the pH be low or high? As H^+ is added, will the pH increase or decrease?). Label the titration curve with letters A-E, and describe the relative quantities of the dissociated base (B^-) and its conjugate acid (HB), as well as the relative quantities of H^+ and OH^- at each point throughout the titration (before the ½ equivalence point [A], at the ½ equivalence point [B], after the ½ equivalence point but before the equivalence point [C], at the equivalence point [D], and after the equivalence point [E]).

2. Suppose you titrated your standard acid (KHP) with the base to be standardized, but added several drops extra of the base (*i.e.* stopped the titration after the phenolphthalein indicator in the solution turned very pink).

    a. How would this affect your final determination of the molarity of the base? Would you calculate the concentration to be greater or less than it really is?
    b. If this calculated value were used to determine the molar mass of the unknown acid, what type of error would you have for the molar mass of the unknown acid? (*i.e.* would you overestimate or underestimate the molar mass value?) Support your answer by, for every step in the calculation, determining whether the calculated value would be greater or less than it should be.