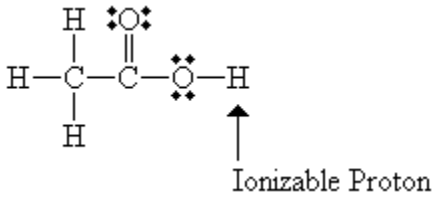
CHEM 122L
General Chemistry Laboratory
Revision 1.5

The Titration of Acetic Acid in Vinegar

- To learn about Volumetric Analysis and Titration.
- To learn about Acetic Acid and Vinegar.
- To learn about Weak Acids.
- To learn about Equilibria involving Weak Acids.

In this laboratory exercise we will determine the percentage Acetic Acid (CH_3CO_2H) in Vinegar. We will do this by Titrating the Acetic Acid present with a Strong Base; Sodium Hydroxide (NaOH). The Endpoint of the Titration will be detected using a Phenolphthalein indicator; an acid-base indicator that changes color from clear to pink in going from its acidic form to its basic form.

Acetic Acid (fr. Latin *acetum* for vinegar) is the main component of Vinegar. It is a carbon based compound with a single ionizable proton, making it an organic acid of the larger class of organic acids called Carboxylic Acids; organic compounds with a –COOH functional moeity.



Alcoholic solutions containing less than 18% Grain Alcohol become Vinegar when airborne bacteria oxidize the Alcohol into Acetic Acid:

$$CH_3CH_2OH_{(aq)} + [O] \longrightarrow CH_3CO_2H_{(aq)} \qquad \text{(Eq. 1)}$$

(Here, [O] is a general notation for any oxidizing agent.) For instance, Cider Vinegar is produced from fermented apples. Balsamic Vinegar is prepared from the *must* of white grapes. White Vinegar is prepared from distilled alcohol. Vinegars are used for a variety of purposes; cooking, cleaning, pickling and gardening. Typically the Acetic Acid content of a vinegar will vary from about 5-8% for Table Vinegars to about 18% for Pickling Vinegars. (Pure Acetic Acid is referred to as *Glacial* Acetic Acid.)

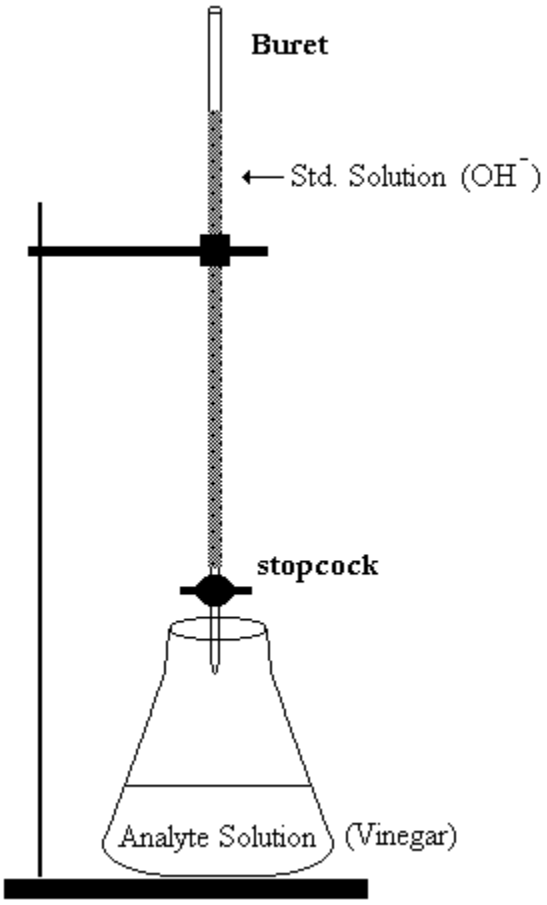
Different Vinegars (http://en.wikipedia.org/wiki/File:Essig-1.jpg)

We will determine the Acetic Acid content of a commercially prepared White Vinegar solution using a type of Volumetric Analysis called Titrimetry.

Volumetric Analyses were late in being developed because accurate methods for measuring volume are difficult to come by.

> According to Francis Holme's book on bleaching, the "value" of pearl ashes was measured in 1756 by noting the number of teaspoonfuls of dilute nitric acid which had to be added before effervescence ceased. This was the first clear instance of using a volumetric approach to chemical analysis ...
>
> The Development of Modern Chemisty
> by Aaron J. Ihde

As noted, a volumetric analysis involves measuring the volume of a solution of known concentration that is needed to completely react with an analyte. In modern cases, a Buret, rather than a teaspoon, is used to deliver the Titrant into the Analyte Solution.



The Titration is performed by slowly adding the titrant to the analyte solution via the buret until an Endpoint is reached. The Endpoint is represented by some distinct physical change in the

analyte solution; typically an Indicator color change, or the cessation of effervescence in the case of the pearl ash titration above. If the indicator is chosen well, the Endpoint will represent the Equivalence Point of the Titration Reaction; the point at which the added amount of titrant is stoichiometrically equivalent to the amount of analyte. By knowing the concentration and volume of the titratnt used, the number of moles titrant can be determined. The reaction stoichiometry then allows us to determine the amount of analyte present.

Suppose we Titrate a solution of Sulfuric Acid (H_2SO_4) with a Standard 0.1054 M Solution of Sodium Hydroxide. The titration reaction is:

$$H_2SO_4(aq) + 2\ NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2\ H_2O$$

Further, suppose 12.56 mL of titrant is required to reach the Endpoint. Then,

$$\#\text{ moles titrant used} = (0.1054\ M) \times (0.01256\ L) = 0.001324\text{ mole NaOH}$$

and:

$$\#\text{ mole } H_2SO_4 = \frac{1\ mole\ H_2SO_4}{2\ moles\ NaOH} \times 0.001324\text{ mole NaOH} = 0.0006619\text{ mole } H_2SO_4$$

Or, in grams:

$$\#\text{ grams } H_2SO_4 = 0.0006619 \times (98.08\ g/mole) = 0.06492\ g$$

In our case, the Analyte is the Acetic Acid in the Vinegar and the Titrant is a dilute solution of the strong base Sodium Hydroxide. The titration reaction is:

$$CH_3CO_2H(aq) + OH^-(aq) \longrightarrow CH_3CO_2^-(aq) + H_2O \qquad \text{(Eq. 2)}$$

The Endpoint of the titration will be detected by observing the color change for a Phenolphthalein indicator added to the Vinegar.

As a Weak Acid, Acetic Acid, only partially ionizes in Water:

$$CH_3CO_2H(aq) + H_2O \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq) \qquad \text{(Eq. 3)}$$

The Equilibrium Constant for this reaction is defined as:

$$K_c = \frac{[CH_3O_2-][H_3O+]}{[CH_3O_2H][H_2O]} \qquad \text{(Eq. 4)}$$

Note, H_2O is included in this expression because, although it is a liquid, it is not a Pure Liquid. However, because the H_2O concentration is large and relatively constant, we frequently define a new constant, K_a, the Acid Dissociation Constant, as:

$$K_a = K_c\,[H_2O] = \frac{[CH_3O_2-][H_3O+]}{[CH_3O_2H]} \qquad \text{(Eq. 5)}$$

For Acetic Acid, this constant has a value of $K_a = 1.8 \times 10^{-5}$, indicating only a small percentage of the Acetic Acid is dissociated in solution.

At the Equivalence Point of the Titration, we have a solution which contains predominately the Acetate Ion ($CH_3CO_2^-$); see (Eq. 2). Because Acetic Acid is a Weak Acid, its Conjugate Base, the Acetate Ion, is also a Weak Base. This means it will partially Hydrolyze in Water to form OH^-:

$$CH_3CO_2^-(aq) + H_2O \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) \qquad \text{(Eq. 6)}$$

This equilibrium can also be quantified by an Equilibrium Constant:

$$K_c = \frac{[CH_3CO_2H][OH^-]}{[CH_3O_2-][H_2O]} \qquad \text{(Eq. 7)}$$

And, again, because the H_2O concentration is large and relatively fixed, we can define a Base Dissociation Constant K_b as:

$$K_b = K_c\,[H_2O] = \frac{[CH_3CO_2H][OH^-]}{[CH_3O_2-]} \qquad \text{(Eq. 8)}$$

For the Acetate Ion, $K_b = 5.56 \times 10^{-10}$.

This is important because it allows us to calculate the expected pH at the Equivalence Point of the Titration. For a Titration that results in a 0.05 M solution of Acetate Ion, we have:

	$CH_3CO_2^-$	CH_3CO_2H	OH^-
I	0.05 M	0 M	0 M
C	- x M	+ x M	+ x M
E	0.05 – x M	x M	x M

Inserting these results into the expression for K_b results in:

$$5.56 \times 10^{-10} = \frac{x^2}{(0.05-x)} \qquad \text{(Eq. 9)}$$

Solving, we obtain $x = 5.27 \times 10^{-6}$ M. Or,

$$[OH^-] = 5.27 \times 10^{-6}\ \text{M} \qquad \text{(Eq. 10)}$$

at the Equivalence Point. The pOH of this solution is given by:

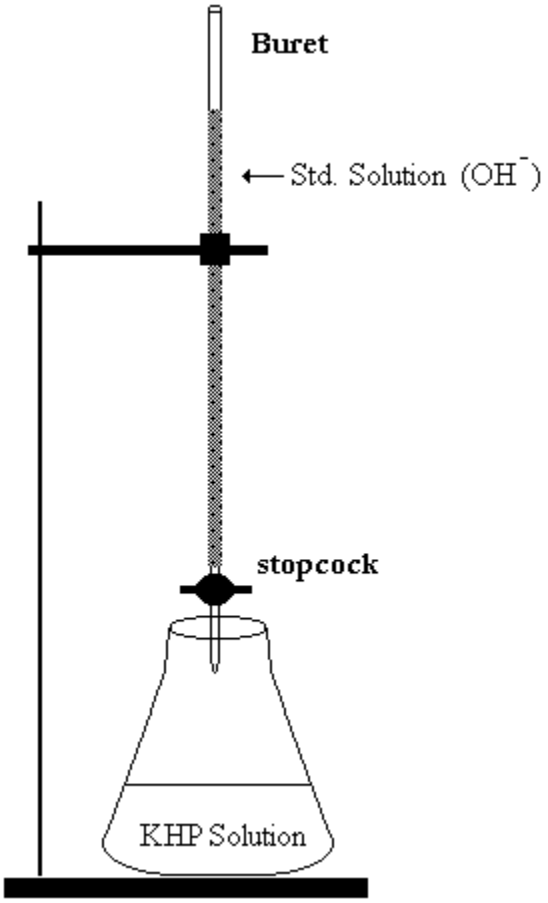
$$pOH = -\log [OH^-] = -\log (5.27 \times 10^{-6}) = 5.28 \qquad \text{(Eq. 11)}$$

which allows us to calculate the pH:

$$pH = 14 - pOH = 14 - 5.28 = 8.72 \qquad \text{(Eq. 12)}$$

In any titration we wish to have the Equivalence Point equal to the Endpoint. For our case, this means we should select an Indicator that changes color near pH = 8.72. (See appendix.) Phenolphthalein will suffice; changing from clear to pink near pH = 8.

One final point needs to be addressed. How do we know the concentration of the OH^- titrant? Although Sodium Hydroxide is a solid, preparation of solutions of accurately known concentration is difficult. The base is very hygroscopic. Additionally, the resulting solution tends to absorb Carbon Dioxide from the air, which neutralizes some of the base. The solution is simple enough, we Standardize the NaOH solution by using it to Titrate a solution of Potassium Hydrogen Phthalate ($KHC_8H_4O_4$), which is frequently abbreviated KHP. Here the KHP is acting as a Primary Standard. Primary Standards are extremely stable solids that can be weighed out very accurately and used to Standardize titrant solutions whose concentration is not accurately known.



The Neutralization reaction for KHP by NaOH is in a one-one mole ratio, so the Titration Reaction is:

$$KHP_{(aq)} + NaOH_{(aq)} \longrightarrow KNaP_{(aq)} + H_2O \qquad \text{(Eq. 13)}$$

By knowing the mass of the KHP, we can determine the number of moles NaOH used in the titration and thus determine its concentration.

Suppose 1.0221g of KHP is titrated with 37.80mL of NaOH. What is the concentration of the NaOH Standard Solution?

mole KHP = (1.0221 g) x (mole KHP / 204.23 g) = 0.005005 mole KHP

mole NaOH = 0.005005 mole KHP x (1 mole NaOH / 1 mole KHP)
= 0.005005 mole NaOH

Molarity = $\frac{\#\ mole\ KHP}{Liters\ Solution} = \frac{0.005005\ mole}{0.03780\ L}$ = 0.1324 M

Thus, we will first prepare a solution of NaOH and Standardize it against KHP. Then, we will use this Standard Solution to Titrate the Vinegar to a Phenolphthalein Endpoint. This will allow us to determine the number of moles Acetic Acid in the Vinegar. And, this can be used to determine the Percentage Acetic Acid.

Pre-Lab Safety Questions

1. When diluting acids, why do we add the acid to Water, and not the other way around?

2. If some base is spilled on your skin, it often results in a "slippery" feeling. Why is this? How long must you flush your skin with Water if you spill a basic solution on yourself?

3. Same question concerning getting base in your eyes?

Procedure

Preparation of approx. 0.1 M NaOH

Prepare 400 mL of an approximately 0.1M solution of NaOH by dilution of the roughly 6M solution provided. Please have your dilution scheme approved by your instructor.

Standardization of NaOH

1. Weigh out ~0.715g of KHP on the glazed papers provided.

2. Transfer this to a 250 mL Erlenmeyer Flask. Wash any residual KHP off the glazed paper into the flask. Dissolve in 50 mL deionized Water.

3. Add a few drops Phenolphthalein.

4. Titrate to the Endpoint with your NaOH solution. Your instructor will indicate how to properly use the Buret. **For the 50mL burets used in this titration, all volume readings can be made with a precision of 0.02 mL. Check with your instructor to make sure you are reading the buret with sufficient precision.**

5. Repeat this process for a total of three trials. **Check with your instructor to make sure the results are sufficiently close to each other.** If the results are not sufficiently close together, repeat the titration a fourth time.

Titration of Vinegar

1. Obtain about 25 mL of Vinegar in a small beaker. Be sure to record the brand and Percentage Acetic Acid reported by the manufacturer.

2. Use a pipet to transfer 4 mL of the Vinegar to a 250 mL Erlenmeyer Flask. Dilute this to about 50 mL with Water.

3. Add a few drops Phenolphthalein.

4. Titrate to the Endpoint with your NaOH solution.

5. Repeat this process for a total of three trials. **Check with your instructor to make sure the results are sufficiently close to each other.** If the results are not sufficiently close together, repeat the titration a fourth time.

Data Analysis

1. Determine the Molarity of the Standard NaOH solution for each of the three trials in the Standardization procedure. Average the results.

2. Determine the mass of Acetic Acid in the Vinegar solution for each of the three trials in the Titration procedure. Average the results.

3. Determine the mass of the Vinegar solution used for each titration. The density of Vinegar is about
   1.005 g/mL.

4. Determine the Percentage Acetic Acid in the Vinegar.

5. Calculate the Percentage Difference between your result and that reported by the manufacturer.

Post Lab Questions

Complete all the questions in the "*Titrator* Titrations" appendix.

Appendix - Acid-Base Indicators

Indicator	Range	Low pH Color	High pH Color
Thymol Blue	1.2 – 2.8	Red	Orange
Methyl Orange	3.1 – 4.4	Red	Yellow
Congo Red	3.0 – 5.0	Purple	Red
Methyl Red	4.8 – 6.0	Red	Yellow
Bromocresol Purple	5.2 – 6.8	Yellow	Purple
Bromthymol Blue	6.0 – 7.6	Yellow	Blue
Cresol Red	7.2 – 8.8	Orange	Red
Thymol Blue	8.0 – 9.6	Yellow	Blue
Phenolphthalein	8.0 – 9.6	Clear	Pink
Alizarin Yellow	10.1 – 12.0	Red	Purple

Appendix - *Titrator* Titrations

In this exercise, we will examine the Titration Curve for a weak acid that is being titrated with a strong base. We will use *Titrator* to generate the Titration Curve for this system; varying the initial concentration of acid as well as the acid's dissociation constant K_a.

Consider the titration of Acetic Acid (HAc), a typical weak acid, with Sodium Hydroxide. The Titration Reaction for this system is:

$$CH_3CO_2H(aq) + OH^-(aq) \longrightarrow CH_3CO_2^-(aq) + H_2O$$

Initially, we start with a system that contains only Acetic Acid and Water and their ionization products, all at equilibrium:

$$HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$$

$$H_2O \rightleftharpoons H^+(aq) + OH^-(aq)$$

As Hydroxide is added via the buret, Acetic Acid is converted to Acetate and these equilibria must be re-established. We can use *Titrator* to determine the concentration of each species once the reactions come to equilibrium. In particular, we wish to determine the equilibrium concentration of H^+ at each point during the titration; a plot of pH versus volume Hydroxide added constitutes the Titration Curve.

We now examine how *Titrator* handles these titration problems. Every time titrant (OH^-) is added to the system (HAc), *Titrator* resolves the equilibrium problem and displays the results in a spreadsheet. The results can also be displayed graphically or downloaded for further analysis.

To establish our *Titrator* definition we will select HAc as a Component; we start with a known Formal Total concentration of this species. H_2O is another natural choice for the Components; its Free concentration is fixed at 55.5M. Also, selecting H^+ as a component makes sense because its removal from HAc and H_2O "forms" both the Ac^- and the OH^-. However, we want to titrate the system with OH^-, which means that this must be a Component. If OH^- is to be our Component choice (why can't both H^+ and OH^- be selected as components?), then we will no longer able to "form" Ac^-. So, in order to select HAc, H_2O and OH^- as Components, we must re-write the first equilibrium in such a way as to form Ac^-. We will do this by compounding both of our equilibria in the following fashion:

$$HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq) \qquad K = 1.7 \times 10^{-5}$$

$$+ H^+(aq) + OH^- \rightleftharpoons (aq)\ H_2O \qquad K = 10^{+14}$$

$$HAc(aq) + OH^-(aq) \rightleftharpoons Ac^-(aq) + H_2O \qquad K = (1.7 \times 10^{-5})(10^{+14}) = 1.7 \times 10^{+9}$$

Now, all is right with the World; OH^- can be used to "form" Ac^- from HAc. It can also form H^+ from H_2O. And, now, we have not over specified the system with too many components.

So, the *Titrator* definition for this system, starting with 0.1F HAc, will be:

Component	Type	Total M	Guess Log Free M	Charge
HAc	Total	0.1	0	0
H_2O	Free	55.5	0	0
OH^-	Total	0	-7	-1

Species	Dissolved/Ppt	logK	ΔH	ΔS		
H^+	Dissolved	-14				
			Coefficients:		OH^-	-1
					H_2O	+1
Ac^-	Dissolved	9.23				
			Coefficients:		OH^-	+1
					HAc	+1
					H_2O	-1

Questions:

1. Use *Titrator* tp determine the pH at the start of the titration?

Now, let's titrate the system with Hydroxide. *Click* on "Titrate". Specify the Titrant composition:

Titrant Composition
- Primary: OH^-
- Concentration: 0.1 M

Set Experimental Volumes
- Initial Sol'n Vol: 25 mL
- Titrant Vol/Addition: 0.5 mL
- Number of Points: 100

Now *click* "Titrate" and display the H^+ concentration as the 2nd Species.

Questions:

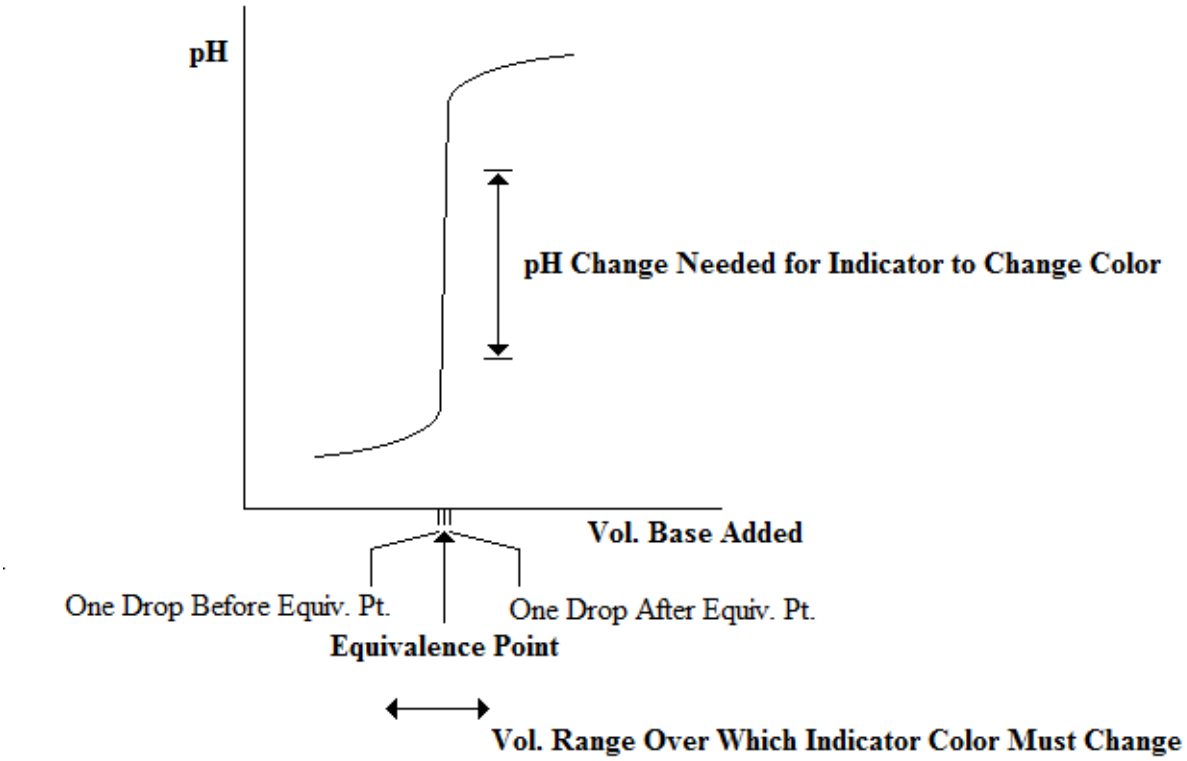
2. Examine the Results Table and determine the pH at the following volumes added:

   12.5 mL
   25.0 mL (Equivalence Pt.)
   50.0 mL

How does the pH at the Equivalence Pt. compare with the transition pH for the indicator Phenolphthalein? Is this a good Indicator choice for this titration? Explain.

3. Use *Titrator's* "Export" feature (under the "File" tab) to save the "Results" table.

Now we can use *Titator* to rapidly generate the titration curve for Acetic Acid systems that become more and more dilute. Basically, in order for a titration to be effective, the pH of the system must change dramatically as the equivalence point is approached. This rapid change in pH will cause an appropriately chosen indicator to change color.



If the pH change is not abrupt over a small volume range near the equivalence point, then the titration will not be effective because the color change of the indicator will be diffuse. So, we want to know if the concentration of the Acetic Acid affects the abruptness of the pH change near the equivalence point as the titration is carried-out.

4. Now change the initial concentration of Acetic Acid and the Hydroxide titrant concentrations to the following values. Generate the Titration Curve for each case. (All other titration parameters should be the same as above.)

Total M for HAc	Titrant Comp. Conc.
0.01	0.01
0.001	0.001
0.0001	0.0001
0.00001	0.00001
0.000001	0.000001

Export each "Results".

5. Upload each case into *Excel* and plot each Titration Curve simultaneously on the same graph.

Note:

i) When uploading the files into *Excel*, indicate that the "Results" files are "Space Delimited".

Volume	HAc	OH-	H2O	H+	Ac-
0.00E+00	9.87E-02	7.72E-12	1.00E+00	1.29E-03	1.29E-03
5.00E-04	9.55E-02	1.60E-11	1.00E+00	6.27E-04	2.59E-03
1.00E-03	9.19E-02	2.70E-11	1.00E+00	3.70E-04	4.22E-03
1.50E-03	8.84E-02	3.94E-11	1.00E+00	2.54E-04	5.91E-03

ii) You will have to manually select the columns containing the H^+ concentrations and the Vol. Titrant added.

iii) You will next need to have *Excel* calculate the pH from the H^+ data.

Volume	H+	pH
0.00E+00	1.29E-03	2.89
5.00E-04	6.27E-04	3.20
1.00E-03	3.70E-04	3.43
1.50E-03	2.54E-04	3.60

iv) Finally, you must tabulate the pH results together in order to plot them.

Volume	pH (0.1M)	pH (0.01M)
0.00E+00	2.89	3.39
5.00E-04	3.20	3.51
1.00E-03	3.43	3.61
1.50E-03	3.60	3.71

6. Qualitatively, what is happening to the Titration Curve? Do we have to worry about our Indicator choice? Will phenolphthalein be an appropriate indicator choice for each of these titrations? Explain.

Now we want to address what happens to the titration curve as the strength of the acid being titrated is decreased. Do we need to worry about the titration becoming ineffective.

7. Return to a system that is 0.1M HAc being titrated with 0.1M OH^-. Decrease the equilibrium constant for the acid. Do this by changing the logK for the formation of Ac^- from 9.23 to:

   8.23, 6.23, 4.23

   Perform Step #5 for this data. Comment on the results.