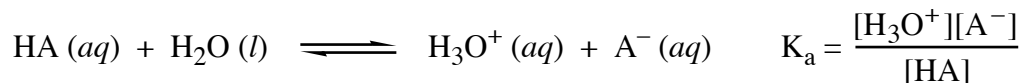# 10

Determination of the K_a Value and Molar Mass of an Unknown Weak Acid

Introduction

In this experiment you will titrate a monoprotic weak acid with a strong base, and measure the titration curve with a pH meter. By analyzing the titration data, you will be able to determine the ionization constant K_a for the weak acid, as well as its molar mass.
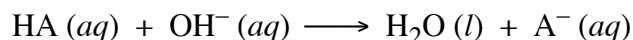
Weak acids react with water to produce small concentrations of ions. The degree of ionization is described by the equilibrium constant K_a.

$$\text{HA } (aq) \text{ + } H_2O \text{ } (l) \rightleftharpoons H_3O^+ \text{ } (aq) \text{ + } A^- \text{ } (aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The value of K_a can be determined experimentally by measuring the concentrations of H_3O^+, A^-, and HA at equilibrium.

To determine K_a, it may seem straightforward to put a measured amount of HA into a measured amount of pure water and measure the pH. From the pH, you could find $[H_3O^+]$, which should be equal to $[A^-]$ because of the one-to-one stoichiometry. By subtraction you could find the remaining [HA], and the calculate K_a. However, there are two flaws in this approach. First, you would need to know the initial concentration of HA, so you would have to do another experiment to find its molar mass. Second, truly pure water is not available in our laboratories. Our water has been deionized, which means it has been passed through a column that replaces metal ion impurities (such as Na^+, Ca^{2+}, and Fe^{3+}) with H_3O^+ ions. On some days, our deionized water has a pH as low as 4! Since weak acids produce very low H_3O^+ concentrations ($\sim10^{-5}$ M for example), starting with pH 4 water would be disastrous. Your result would be off by a factor of 100!

In this experiment, you will prepare a solution whose pH is resistant to impurities by titrating the weak acid (we'll call it HA) with a strong base.

$$\text{HA } (aq) \text{ + } OH^- \text{ } (aq) \longrightarrow H_2O \text{ } (l) \text{ + } A^- \text{ } (aq)$$

This reaction has a very large equilibrium constant and goes to completion. Every mole of added OH^- ions converts one mole of HA to one mole of its conjugate base, A^-.

At the *equivalence point* of a titration, exactly enough OH^- ions have been added to react with all of the HA molecules that were originally present. Around this point, the
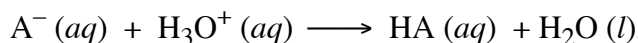
pH of the mixture increases suddenly and dramatically. The rapid increase in pH can be detected using an indicator (such as phenolphthalein) or with a pH meter. If you measure the amount of OH^- needed to reach the equivalence point, you also know the moles of HA that were present originally.

The *halfway point* of a titration is halfway to the equivalence point. Enough OH^- ions have been added to react with exactly half of the HA molecules that were originally present, converting them into A^-. At this point, there are equal amounts of HA and A^- in the solution. At the halfway point, the K_a expression simplifies to:
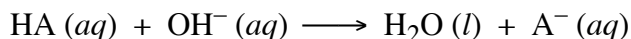
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = [H_3O^+] \text{ when } [HA] = [A^-]$$

If you measure the pH at the halfway point, you can easily calculate $[H_3O^+]$ and K_a for the acid.

The halfway point lies in the middle of the *buffer region* of the titration curve. In the buffer region, there are appreciable concentrations of both HA and A^- ion the solution. While the concentrations are equal at the halfway point, they are within the same order of magnitude throughout the buffer region. In the buffer region, the pH is insensitive to acidic impurities in our laboratory water, because A^- is available to react with them.

$$A^- \ (aq) \ + \ H_3O^+ \ (aq) \ \longrightarrow \ HA \ (aq) \ + H_2O \ (l)$$

Thus, a pH measurement at the halfway point of your titration should most accurately reflect the strength of your unknown acid. Buffer solutions have a similar resistance to pH changes from small amounts of basic impurities, because HA is available to react with them.

$$HA \ (aq) \ + \ OH^- \ (aq) \ \longrightarrow \ H_2O \ (l) \ + \ A^- \ (aq)$$

Example to show how the pH of buffer solutions is insensitive to small amounts of impurity:

Suppose at the halfway point of the titration, your solution has $[HA] = [A^-] = 0.04$ M.

The pH 4 laboratory water has $[H_3O^+] = 0.0001$ M.

After the impurity reacts with A^-,

   $[A^-] = 0.04 \text{ M} - 0.0001 \text{ M} = 0.0399 \text{ M}$,

   $[HA] = 0.04 \text{ M} + 0.0001 \text{ M} = 0.0401 \text{ M}$, so

   $$[H_3O^+] = \frac{K_a[HA]}{[A^-]} = \frac{K_a(0.0401)}{(0.0399)} = 1.005 \, K_a \ (< 1\% \text{ different}), \text{ and}$$

   $pH = -\log (1.005 \, K_a) = K_a - 0.002$ (off by only 0.002 pH units).

Procedure

> **SAFETY PRECAUTIONS:** Wear your SAFETY GOGGLES. If you spill any acid or base on your skin or clothing, wash it off immediately with copious amounts of running water.
>
> **WASTE DISPOSAL:** Pour the excess NaOH and buffer solutions down the drain, followed by plenty of running water. Empty the titrated solutions and the remainder of your unknown acid solution into the INORGANIC WASTE containers in the fume hood.

Part I. *Preparing a solution of your unknown weak acid*

Obtain a vial containing an unknown weak acid. Your unknown will be a solid. Record the unknown number.

Obtain a 100.0-mL volumetric flask and a powder funnel. Weigh the vial containing the unknown on the analytical balance, and record its mass to ±0.001 g. Place the funnel in the neck of the volumetric flask. Gently tap between 1.9 and 2.1 grams of the unknown into the funnel. (You will need to check the mass of the vial several times to see how much you have added.) Reweigh the vial, and record its final mass to ±0.001 g. The difference in mass is the mass of unknown acid in your flask.

Use a jet of deionized water from a wash bottle to rinse all the acid from the funnel into the volumetric flask. Fill the flask about three quarters full with deionized water. Swirl until all the acid dissolves. (This may take a while.) Then add deionized water just up to the 100.0-mL mark. Invert the flask several times for the final mixing.

The concentration of the solution you have just prepared is somewhere in the range 0.09 M – 0.2 M.

Part II. *Performing a trial titration using phenolphthalein indicator*

Obtain about 100 mL of standardized NaOH solution in a clean dry flask or beaker. Record the exact concentration of the NaOH solution. It is best to keep this solution covered when you are not using it. Rinse out a buret three times with 5-mL portions of the NaOH solution. Tilt the buret back and forth, so the solution touches every part of the inside walls, and remember to run some solution through the tip. Then fill the buret to just under the 0.00-mL mark with the NaOH solution. Support it on a ring stand using a buret clamp.

Rinse out a 25.00-mL pipet three times with small portions of your unknown acid solution. Pipet exactly 25.00 mL of your unknown acid solution into a clean Erlenmeyer flask. (This flask does not have to be dry.) Add 3 drops of phenolphthalein indicator. Place the flask under the buret, and place a piece of white paper under the flask.

Read the NaOH buret and record the reading to ±0.01 mL. Titrate the acid solution with NaOH, swirling the flask constantly. The endpoint is the first sign of pink color that persists for at least 60 seconds before fading away. As you near the endpoint, add the NaOH drop by drop. At the endpoint, read the NaOH buret and record the reading to ±0.01 mL. The endpoint is very close to the equivalence point of the titration.

Preparing for the pH measurements: The trial titration has provided information that will help you measure the titration curve properly. The pH changes rapidly near the beginning of the titration and near the equivalence point. You will need closely spaced pH measurements in these regions. From the trial titration, you know how many milliliters of NaOH solution are needed to reach the endpoint. Calculate 10%, 90%, 110%, and 120% of this volume.

Part III. Determining the titration curve

Obtain a pH meter and set it up at your bench. Calibrate the pH meter according to the instructions for that particular pH meter. Be careful with the glass tip of the electrode, as it is very delicate and very expensive. Do not let it dry out, and remember to rinse it with deionized water when transferring it from one solution to another.

Refill the buret with NaOH solution to just under the 0.00-mL mark. Record the initial reading of the buret to ±0.01 mL. Pipet exactly 25.00 mL of your unknown acid solution into a clean, dry 150-mL beaker. Add 3 drops of phenolphthalein indicator. Measure the pH of the solution.

You will now add small amounts of NaOH to your unknown acid solution. After every addition, you should stir the mixture with the pH electrode, read the pH, and read the buret to ±0.01 mL.

At the beginning of the titration (0–10% of the way to the endpoint), take readings after every 5 drops of NaOH added.

In the middle of the titration (10–90% of the way to the endpoint), take readings after every milliliter of NaOH added.

Near the endpoint of the titration (90–110% of the way to the endpoint), start by taking readings after every 5 drops of NaOH added. When the pH starts to change by more than 0.2 pH units between additions, take a reading after every drop of NaOH added. At an equal distance on the opposite side of the endpoint, you may again take readings after every 5 drops of NaOH added.

Beyond the endpoint of the titration (110–120% of way to the endpoint), take readings after every milliliter of NaOH added.
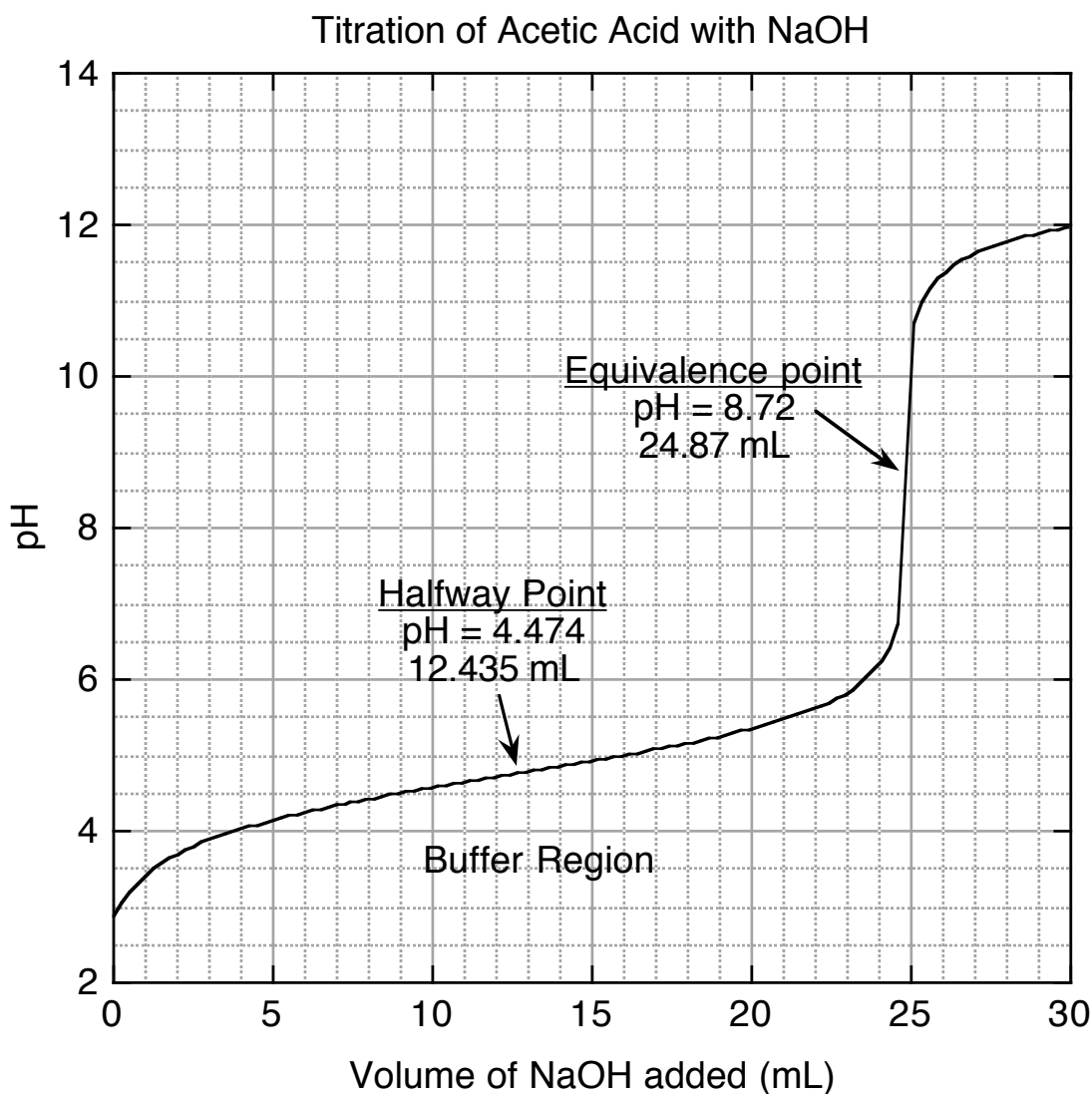
After completing the experiment, remember to rinse out the buret, pipet, powder funnel, and volumetric flask with tap water and return them to the appropriate boxes in the fume hood. Turn off the pH meter, rinse off the electrode and replace its protective cover, and return the pH meter to the fume hood.

Calculations

Make a table of the pH measurements and the milliliters of NaOH solution added in Part C. (To find the milliliters of NaOH added at each data point, you will need to subtract the initial buret reading from each of the other buret readings.)

Prepare a titration curve from your data. That is, make a full page graph with pH on the y-axis and volume of NaOH added on the x-axis. Draw a smooth curve through all the plotted points. On your titration curve, indicate the exact *equivalence point* and *halfway point*, as described on the next two pages.

An example of a titration curve is show below. Your titration curve will not look exactly the same as this one, because you are using a different acid, and different concentrations of acid and NaOH.
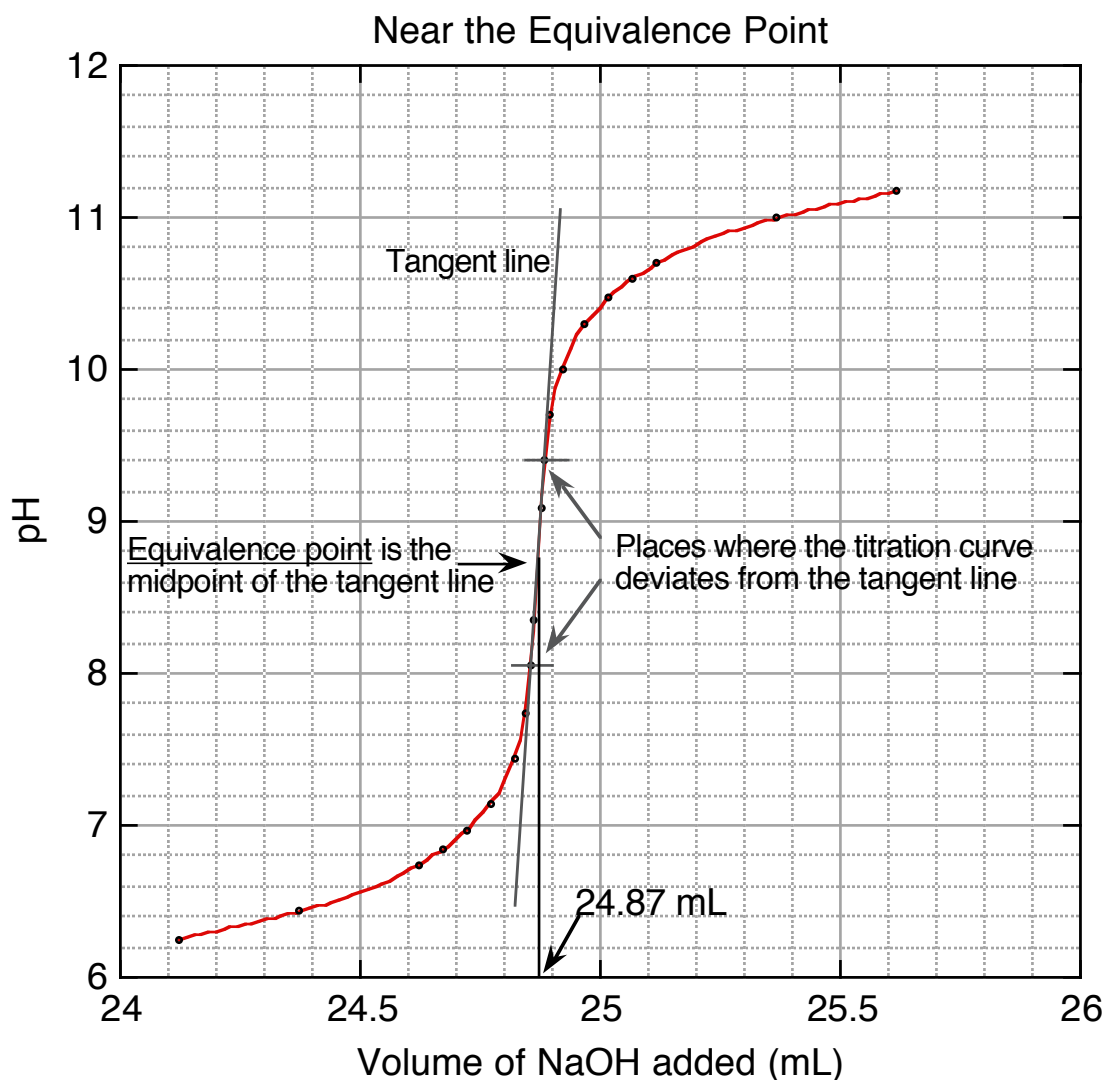
Titration of Acetic Acid with NaOH

Equivalence point
pH = 8.72
24.87 mL

Halfway Point
pH = 4.474
12.435 mL

Buffer Region

pH (y-axis)

Volume of NaOH added (mL) (x-axis)

48

Equivalence point. The *equivalence point* of the titration is the point when exactly enough OH^- ions have been added to react with all of the HA that was originally present. It is the point of inflection in the part of the titration curve where the pH shoots straight up. The *endpoint* of the titration is the point where the indicator changes color. While the endpoint is very close to the equivalence point, they are not exactly the same.

To find the exact volume of NaOH needed to reach the equivalence point, replot the small region of the titration curve around this point. Draw a tangent line that touches the steepest part of the titration curve. Find the two points where the titration curve deviates from the tangent line. The equivalence point is exactly halfway between these two points.

In your experiment, what volume of NaOH was needed to reach the equivalance point? What was the pH at this point?

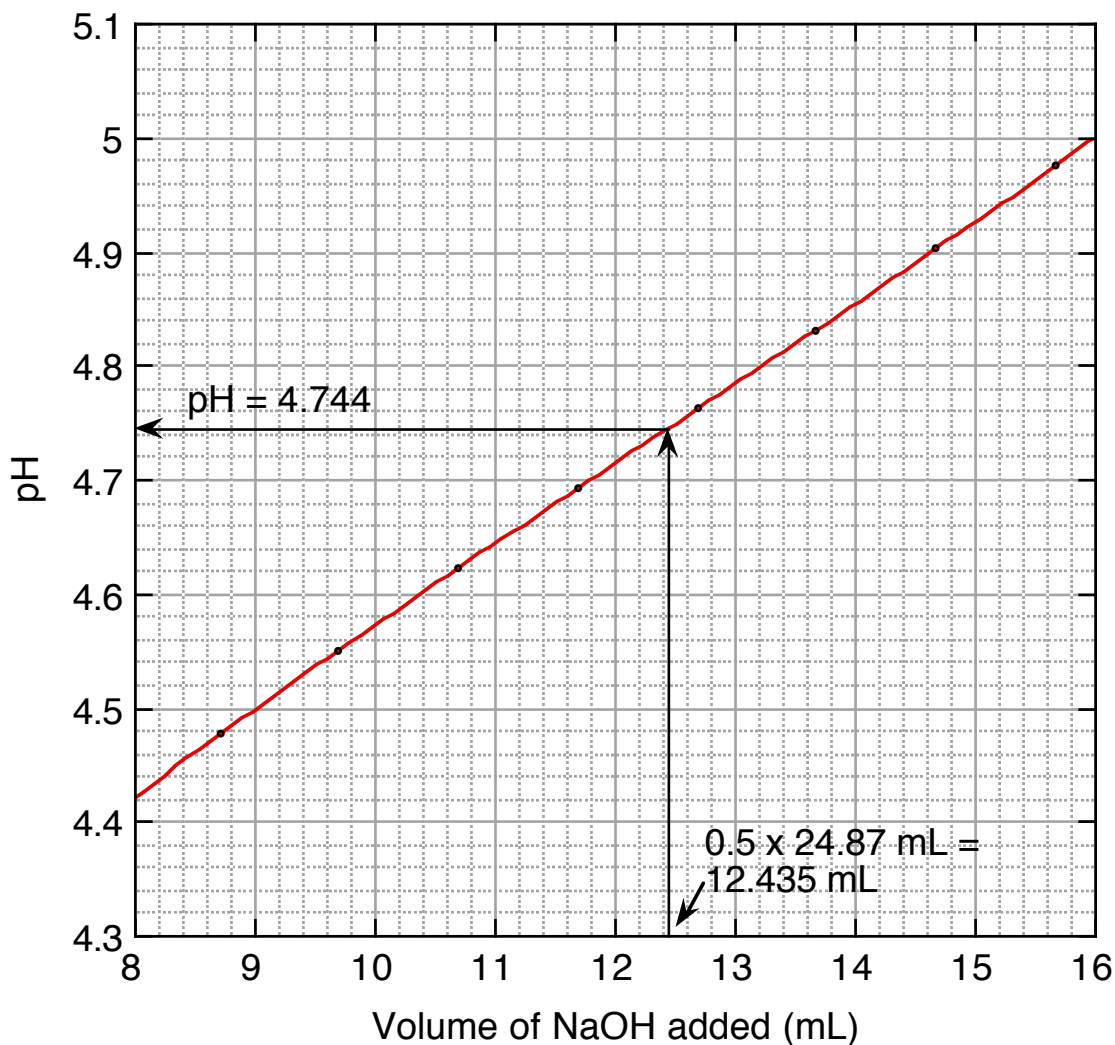How close was the endpoint to the equivalence point in your experiment?

Near the Equivalence Point

Halfway point. The *halfway point* of the titration is the point when enough OH⁻ ions have been added to react with exactly half of the HA that was originally present. If you know the volume of NaOH needed to reach the equivalence point, simply divide it by two for the volume of NaOH needed to reach the halfway point.

To find the exact pH at the halfway point of your titration, replot the region of the titration curve around this point, using an expanded pH scale. This allows a precise interpolation of the pH.

In your experiment, what was the pH at the halfway point?

Near the Halfway Point

pH = 4.744

0.5×24.87 mL = 12.435 mL

Properties of Your Unknown Acid

Now that you have properly located the equivalence point and the halfway point on your titration curve, you are ready to use it to determine the properties of your unknown acid.

1. What is the value of K_a for your unknown acid?
2. What was the concentration of the unknown acid solution you prepared? (Use your titration data and the molarity of the standardized NaOH solution.)
3. What is the molar mass of your unknown acid? (Use the mass and moles of the sample in your experiment.)

Note that the unknown weak acid is not one of the ones in tabulated in your textbook, so you will not be able to identify it.

Checking Your Results for Consistency

Using your experimental K_a value, the concentration of your unknown acid solution and the concentration of the standardized NaOH solution, <u>calculate</u> the pH of the following points on your titration curve:
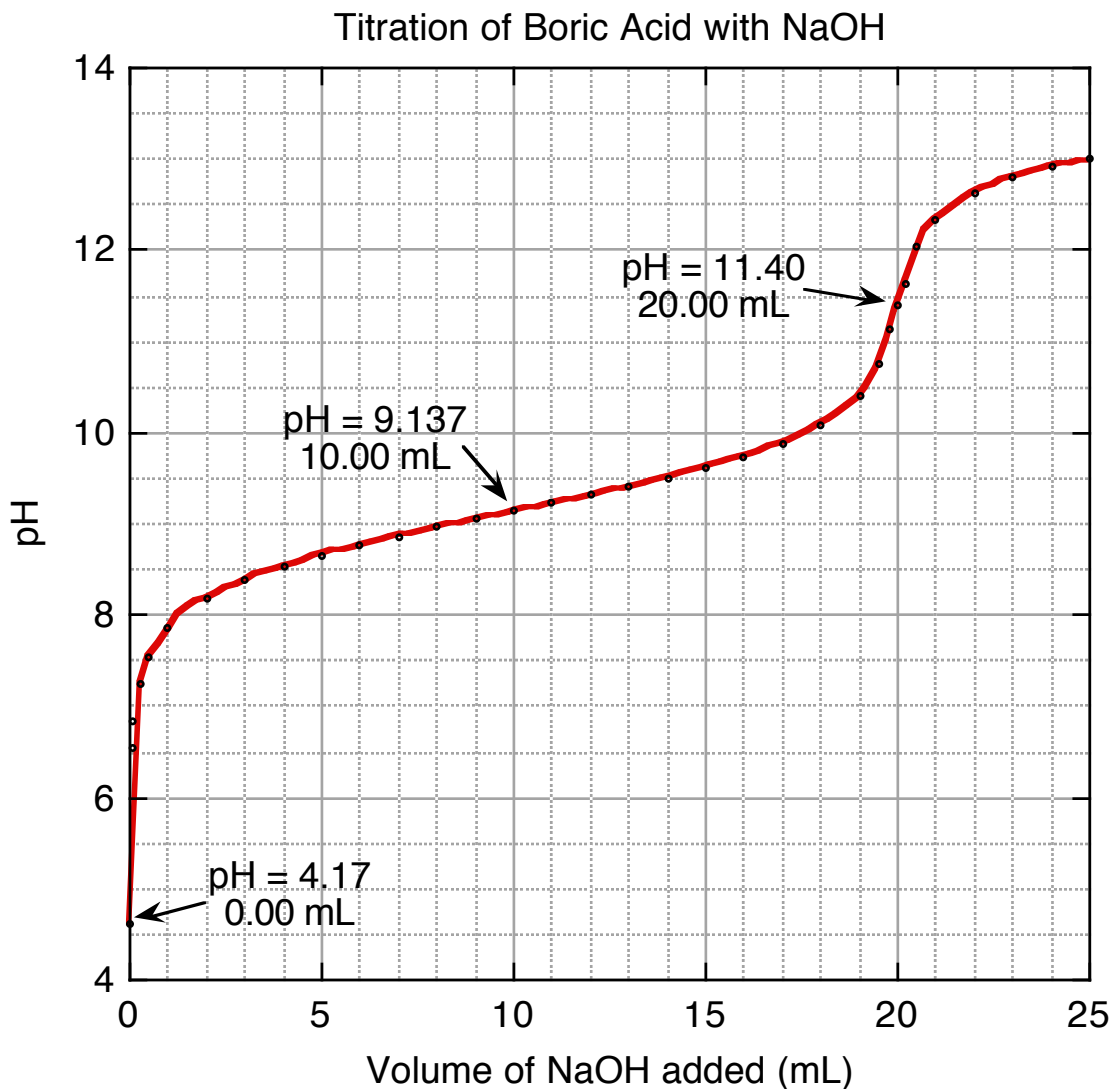
1. The beginning of the titration before any NaOH was added.
2. 25% of the way to the equivalence point
3. 75% of the way to the equivalence point
4. The equivalence point
5. 120% of the way to the equivalence point

Compare the calculated pH values to the pH the values on your graph. Some points will agree better than others. What are the reasons for this?

Prelab Question

The titration curve below was obtained by titrating 25.00 mL of a boric acid solution with a 1.000 M NaOH solution. Use the information given on the titration curve to answer the following questions:

1. What is the value of K_a for boric acid?
2. Is boric acid a stronger or weaker acid than acetic acid?
3. What was the concentration of the original boric acid solution?

Titration of Boric Acid with NaOH

Answers: (1) 7.29×10^{-10}; (2) weaker; (3) 0.8000 M. <u>Show</u> your work and <u>explain</u> your reasoning.