

Experiment 6

Titration II – Acid Dissociation Constant

Introduction:

An acid/base titration can be monitored with an indicator or with a pH meter. In either case, the goal is to determine the equivalence point of the titration. This is the point at which enough titrant has been added to the analyte to just exactly neutralize the analyte. In this experiment, knowledge of the equivalence point will be used to obtain information about the acid dissociation constant, K_a , of the acid being titrated.

When an indicator is used in a titration, the color change occurs at what is called the endpoint. If the indicator has been properly selected, this point will be the same as the equivalence point. When a pH meter is used, the pH of the solution is recorded as the titrant is added. The pH versus the volume of titrant added can be plotted on what is called a *titration curve*. In this case the equivalence point occurs at the point where very small additions of titrant cause a very rapid rise in the pH. Graphically, it is also the point on the curve where the slope, $\Delta\text{pH}/\Delta V$, changes from positive to negative (called the *inflection point*.) Figure 1 is a titration curve for the titration of HCl by NaOH, a strong acid and strong base, where 25.0 mL of 0.1 M HCl is titrated with 0.1 M NaOH.

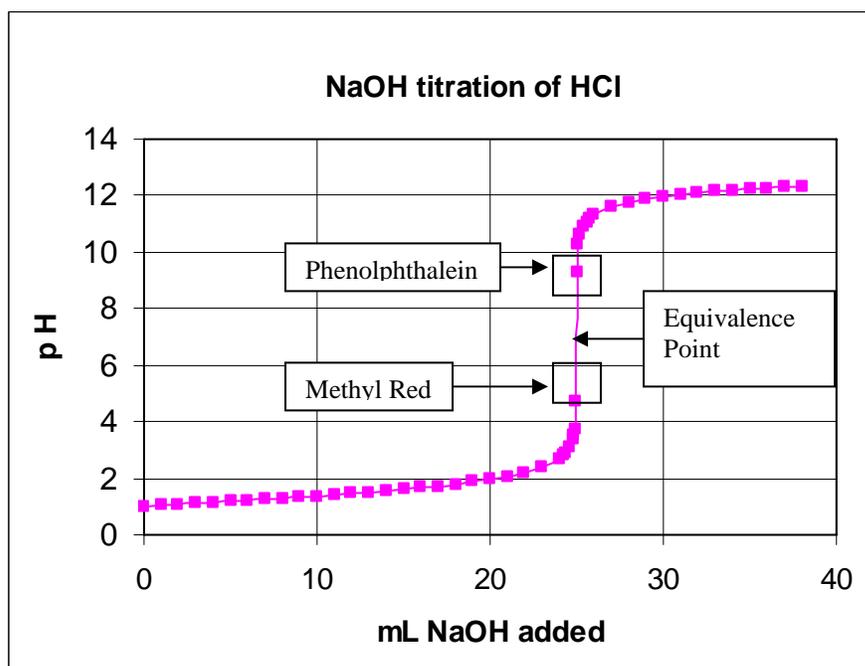


Figure 1. Titration of 25.0 mL of 0.1M HCl by 0.1 M NaOH. Blocked areas on the curve indicate the pH range in which phenolphthalein and methyl red change colors.

Note that the slope, $\Delta\text{pH}/\Delta V$, becomes large when the volume of NaOH added is at 25 mL, so this is the equivalence point. Because of this rapid rise through a range of pH values when the equivalence point is reached, a wide variety of indicators may be used to detect the

endpoint visually. Either methyl red or phenolphthalein can be used for an HCl/NaOH analysis, since both will exhibit color changes in the range of pH values at the equivalence point. Also note that if the slope, $\Delta\text{pH}/\Delta V$, is plotted versus the volume of titrant added, the inflection point will appear as a spike. This is the most precise method for determining the equivalence point, and it is shown in Figure 2 below.

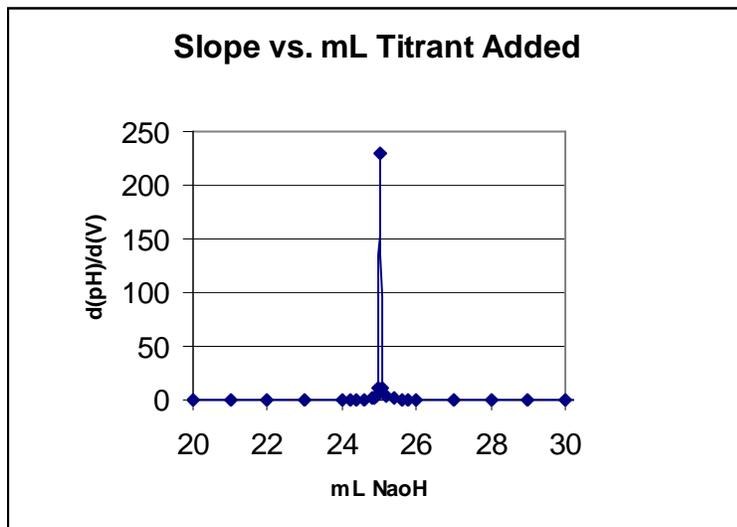


Figure 2. Plot of slope, $\Delta\text{pH}/\Delta V$, vs. mL NaOH from 20 to 30 mL based on Figure 1 titration.

When a **weak acid** is titrated by a strong base, the fact that, in aqueous solution, the weak acid dissociates into a hydrogen ion and the **conjugate base** of the acid changes the appearance of the titration curve. The curve will look similar to Figure 3, which represents the titration of 0.1 M acetic acid with 0.1 M NaOH.

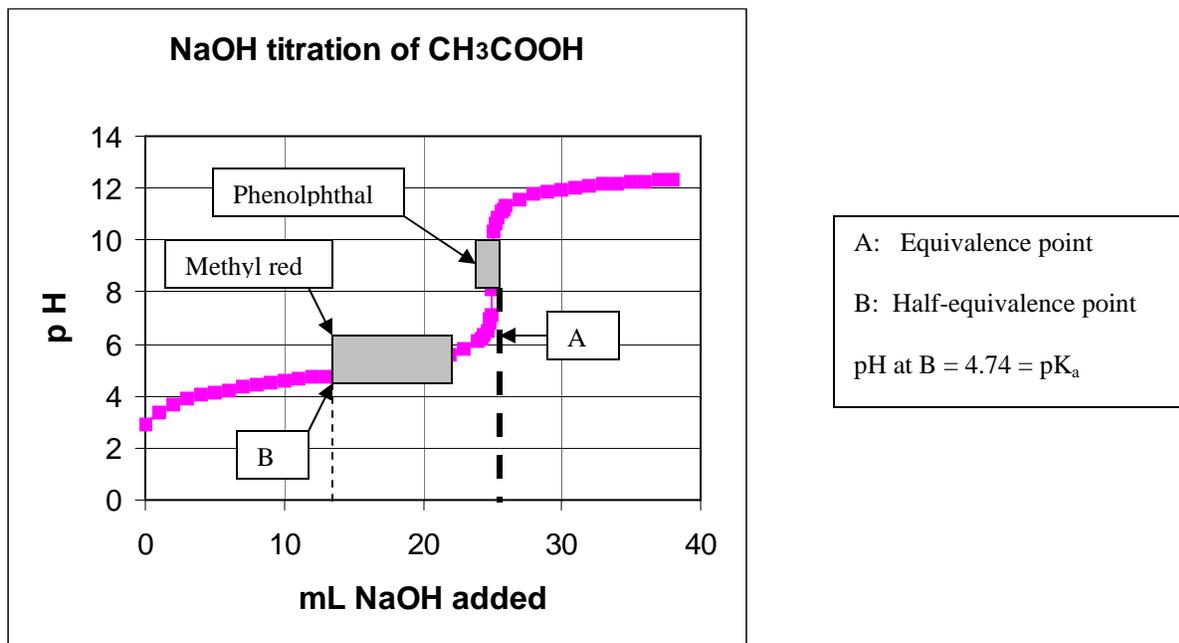


Figure 3. Titration of 25 mL of 0.1M acetic acid by 0.1M NaOH.

Several differences are readily apparent in the comparison of Figures 1 and 3. There are variations in the initial pH, the rate of pH change, and the pH at the equivalence point. The addition of a strong base to a weak acid creates a build up of the salt of the weak acid (in this case, NaCH_3COO) producing a buffering effect, which causes resistance to change in pH. Also, the pH of the equivalence point corresponds to the pH of the conjugate base, CH_3COO^- , which hydrolyzes in water. Notice that the endpoint of the methyl red does not occur at the equivalence point, and therefore it could not be used in the titration. The phenolphthalein is appropriate for this specific titration. All these effects are related to the strength (or degree of dissociation) of the acid being titrated. Because of the incomplete dissociation of the acid, the reaction is in equilibrium, with an acid dissociation constant, K_a , which is specific to that acid.

For the dissociation of any weak acid, HA:



there is an acid dissociation constant, K_a :

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

This can be rearranged to solve for $[\text{H}^+]$:

$$[\text{H}^+] = \frac{K_a [\text{HA}]}{[\text{A}^-]}$$

Using the definition of pH, this equation can be rearranged as follows:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log K_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right), \text{ or}$$

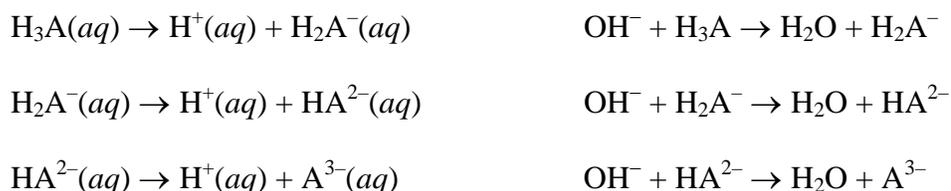
$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

This last expression is known as the *Henderson-Hasselbach equation*. It can be used to calculate the $\text{p}K_a$ (and thus K_a) of an acid. At the equivalence point, the volume of base added is just enough to exactly neutralize all of the acid. At one-half of this volume of added base, called the *half-equivalence point*, enough has been added to neutralize half of the acid. Since half of the acid reacted to form A^- , the concentrations of A^- and HA at the half-equivalence point are the same. Therefore, at the half-equivalence point, the pH is equal to the $\text{p}K_a$.

Since $\log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = \log(1) = 0$, it follows that $\text{pH} = \text{p}K_a$.

A plot of the titration curve allows the equivalence point to be determined. At exactly one-half the volume of the equivalence point, the measured pH is equal to pK_a as illustrated in Figure 3.

For polyprotic acids there are multiple dissociation steps and equivalence points, one for each acidic hydrogen present. The dissociation reactions of a weak polyprotic acid, H_3A , are shown below along with the neutralization reactions that occur in a titration by a strong base.



Each step has a separate dissociation constant: K_{a1} , K_{a2} , and K_{a3} . A titration curve for a triprotic acid is thus expected to have three equivalence points, but often only shows two. A titration curve for a diprotic acid, H_2A , would show two equivalence points, one in which OH^- neutralizes H_2A and a second in which OH^- neutralizes HA^- . The pK_a is obtained in the same way as for a monoprotic acid, but in this case at least two half-equivalence points are present. One half-equivalence point occurs at one-half the volume of the first equivalence point, at which $pH = pK_{a1}$. The second occurs at the volume that is at the midpoint between the first and second equivalence points, and at that point, $pH = pK_{a2}$.

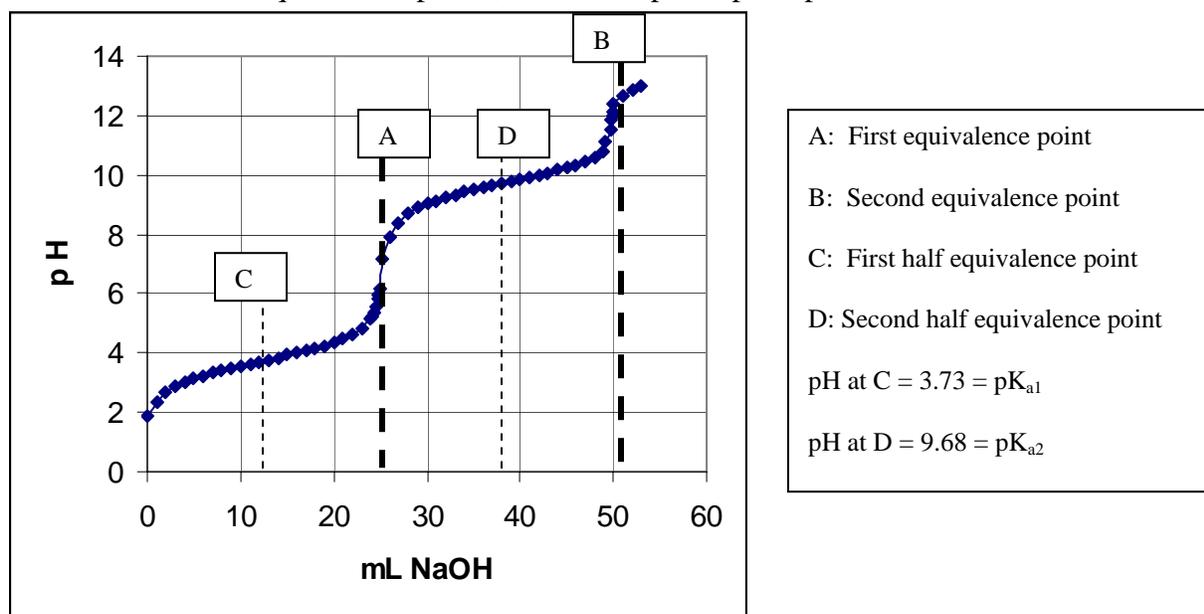


Figure 4. Titration curve of weak diprotic acid by $NaOH(aq)$.

Pre-Lab Notebook: Provide a title, purpose, $CH_3COOH / NaOH$ reaction, brief summary of the procedure, and table of reagents ($NaOH$ and CH_3COOH).

Equipment:

50 mL Buret	Vernier pH Probe
250 mL Beakers (2)	Vernier LabPro
25.00 mL Volumetric Pipet	TI-84 Calculator
25.00 mL Pipet and Bulb	Stir Bar and Stir Plate
DI water	
Ring stand, buret clamp, clamp for pH probe	

In-Lab Procedure:

Note: **Work in pairs.**

Use the standardized NaOH solution prepared during the last lab period. Set up the Vernier system in DATAMATE according to the Vernier tutorial with the pH probe connected to channel 1. Calibrate the electrode as described in Experiment 4.

Part A: Titration of Acetic Acid with NaOH*Phenolphthalein:*

1. Fill the buret with 0.1M NaOH. Pipet 25.00 mL of 0.1 M CH₃COOH into a 250 mL beaker and add 3–4 drops of phenolphthalein indicator. Place the beaker on a white paper towel to best observe color changes.
2. Titrate the solution by adding the NaOH titrant in 1–2 mL increments. Carefully swirl the beaker with each addition.
3. The colored form of the phenolphthalein will begin to stay for a while and then disappear. At this point add the NaOH dropwise until the acetic acid is a very light color. This is the endpoint for phenolphthalein.
4. Measure and record the pH of the solution in the beaker at this end point. Then rinse the pH probe with DI water and replace the probe tip into its vial.
5. Record any color change observed during the titration in your laboratory notebook. The pH and added NaOH volume at that indicator's endpoint should be used to estimate the target point when conducting the following procedure.

Making a Titration Curve:

1. Rinse and thoroughly dry the two 250 mL beakers. Refill the buret to the 0.00 mL mark with 0.1 M NaOH.
2. Pipet 25.00 mL of 0.1 M CH₃COOH into a 250 mL beaker. Place a stir bar in the beaker, and place the beaker on a stir plate.
3. Set up a ring stand with a buret clamp and another clamp to hold the pH probe. Stir the solution on a low setting throughout the titration. Ensure that the probe tip is completely immersed in the acetic acid.
4. Set up the Vernier system to take a pH reading after each volume of NaOH is added. On the main screen select "1" for SETUP. Select "6" for TIME GRAPH, "3" for EVENTS WITH ENTRY, and then "1" for OK. At the main screen press "2" to START data collection.
5. When the pH stabilizes (**and before adding any NaOH**), press ENTER and type in "0" as the buret volume in mL. Then add the NaOH in increments of 1-2 mL (recording the pH by pressing ENTER at each new total volume of NaOH added and

then entering the buret reading). Continue until the volume added and pH approach the values at the endpoint you determined with the phenolphthalein. When the pH nears this value, add the NaOH in 0.5 and finally 0.2 mL increments. When the pH passes the equivalence point, add the NaOH again in 1-2 mL increments until you have added 35 mL.

6. You should have taken approximately 30 data points. Press STO> when you have finished collecting data.
7. Transfer your data to the Logger *Pro* program and transfer the pH/volume data to an Excel file for later analysis. Store the volumes in the A column and the pH values in the B column of the spreadsheet, beginning in cells A1 and B1.

Part B: Titration of an Unknown Polyprotic Acid with NaOH

1. Transfer 15.00 mL of an unknown 0.1 M acid solution to a 250 mL beaker with a 15.00 mL volumetric pipet you have pre-rinsed with a small amount of the solution.
2. Fill a buret to the 0.00 mL mark with standardized NaOH.
3. Rinse the pH meter with DI water. Set up a titration as you did for Part A using the Vernier equipment to measure the pH in the EVENTS WITH ENTRY mode
4. Titrate the unknown acid with NaOH using 1 mL increments of the base except near the first endpoint (as indicated by the more rapid rise in pH) where the increments should be 0.2 mL. After the first endpoint, increase the increments to 1 mL until the second end point is approached. Continue the titration until the second end point has been passed by about 5 mL of added NaOH
5. Transfer this data into Logger *Pro* as before and save it to an Excel file (volume in column A and pH in column B) under a different name for later analysis.

For Next Lab: Prepare both the saturated $\text{Ca}(\text{OH})_2$ and the saturated $\text{Ca}(\text{OH})_2$ with $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ solutions according to the directions given in Experiment #7. Cover with Parafilm for use during next lab.

Treatment of Data:

Part A: Titration of Acetic Acid with NaOH

1. Using the saved data in your Excel file prepare a plot of pH vs. Volume of NaOH added to observe the equivalence point and half equivalence point.
2. To verify the equivalence point, determine the inflection point by calculating the change in pH per change in volume, $\Delta\text{pH}/\Delta V$, for each recorded volume, as shown in Figure 2 for the NaOH/HCl titration. Plot $\Delta\text{pH}/\Delta V$ vs. the volume of titrant added. To perform this, check that your volume and pH values are in columns A and B on your Excel spreadsheet. In cell C1, type: $=(A1+A2)/2$. Click on cell C1 and drag down to the C cell that is on the same row as the last filled cell in columns A and B. Column C now contains the average volume of titrant between two readings.
3. In cell D1, type: $=(B2-B1)/(A2-A1)$ which will calculate the $\Delta\text{pH}/\Delta V$ values. Highlight cell D1 and drag to fill the remaining cells as you did with column C. Column D now contains the values of $\Delta\text{pH}/\Delta V$ for each volume reading. The inflection point is found by plotting $\Delta\text{pH}/\Delta V$ versus the volumes in column C.
4. Once the volume at the equivalence point is known, the volume of the half-

equivalence point can be found. Using the titration curve, the pH at this volume can be determined as shown in Figure 3. Thus pK_a and hence K_a for acetic acid can be calculated. Compare this to the literature value (1.8×10^{-5}).

Part B: Titration of an Unknown Acid with NaOH

- To find the inflection points and half-inflection points for the unknown acid, use the same method as above. Refer to Figure 4 to see how the values of pK_{a1} and pK_{a2} are related to the pH values at the two half-inflection points.
- Calculate K_{a1} and K_{a2} from pK_{a1} and pK_{a2} and identify the unknown by comparison with the K_{a1} and K_{a2} values for polyprotic acids listed in the table below.

Acid	K_{a1}	K_{a2}	K_{a3}
Boric, H_3BO_3	7.3×10^{-10}	1.8×10^{-13}	1.6×10^{-14}
Carbonic, H_2CO_3	4.2×10^{-7}	4.8×10^{-11}	
Citric, $H_3C_6H_5O_7$	7.4×10^{-3}	1.7×10^{-5}	4.0×10^{-7}
Hydrosulfuric, H_2S	1×10^{-7}	1×10^{-19}	
Oxalic, $H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric, H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	3.6×10^{-13}
Phosphorous, H_3PO_3	1.6×10^{-2}	7.0×10^{-7}	

Lab Report Outline for Titration II

Graded Sections of Report

Percent of Grade

Pre-Lab	10
In-Lab	10
Post-Lab	
Part A: Titration of Acetic Acid with NaOH	
1. Attach an Excel plot of pH vs. volume of NaOH added.	10
2. Attach a plot of $\Delta pH/\Delta V$ versus the average volume of NaOH added.	10
3. State "The volume at the half-equivalence point is _____. The pH at the half-equivalence point is _____. Thus K_a for acetic acid is _____."	15
Part B: Titration of an Unknown Polyprotic Acid with NaOH	
1. Attach an Excel plot of pH vs. volume of NaOH added.	10
2. Attach a plot of $\Delta pH/\Delta V$ versus the average volume of NaOH added.	10
3. Complete a table as shown below. In the entry " K_{a1} and K_{a2} from Text table," enter the values from the table that correspond most closely to your experimental value. Then state: "The unknown polyprotic acid is _____."	15

	First	Second
Equivalence point volume (mL NaOH)		
Half-equivalence point volume (mL NaOH)		
Equivalence point pH		
Half-equivalence point pH		
K_{a1} and K_{a2} experimental		
K_{a1} and K_{a2} from Text table		

4. Was the equivalence point determined from the end point of the titration with phenolphthalein the same as the one determined by the plot of $\Delta\text{pH}/\Delta V$ versus the average volume of NaOH added? Discuss any difference. 5
5. Explain why methyl red could not be used as an indicator for the NaOH titration of acetic acid. 5