

Acid Dissociation Constants and the Titration of a Weak Acid

One of the most important applications of equilibria is the chemistry of acids and bases. The Brønsted-Lowry acid-base theory defines an acid as a species that donates a proton and a base as a species that accepts a proton. In the case of an aqueous solution of a strong acid, such as HCl, the acid reacts completely with the water and dissociates into the hydronium ion, H_3O^+ , and the chloride ion, Cl^- as shown by



In this reaction, HCl is the Brønsted-Lowry acid and H_2O is the Brønsted-Lowry base. In an aqueous solution of HCl, the associated species, HCl, does not exist. The species present are H_3O^+ , Cl^- , and H_2O . Since this reaction essentially goes to completion, a single-headed arrow pointing to the right is used in the chemical equation.

Unlike strong acids, aqueous solutions of weak acids do not completely dissociate into the hydronium ion and the corresponding anion but instead reach equilibrium. If we let HA symbolize a weak acid, then the equilibrium reaction of a weak acid with water is represented by



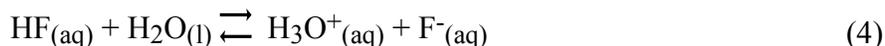
Similarly, in this reaction HA is the Brønsted-Lowry acid and H_2O is the Brønsted-Lowry base. In an aqueous solution of HA, the species present are the associated species, HA, the hydronium ion, H_3O^+ , the anion A^- , and H_2O . Note that double arrows pointing in opposite directions are used in the chemical equation since this reaction does not go to completion but instead reaches equilibrium.

HA and A^- are also referred to as a conjugate acid-base pair where HA is the acid and A^- is its conjugate base, formed when HA donates its proton. The species A^- is considered to also be a Brønsted-Lowry base since it can accept a proton. The species that make up a conjugate acid-base pair only differ in structure by the presence of a single proton, H^+ . Likewise, H_2O and H_3O^+ also constitute a conjugate acid-base pair where H_3O^+ is the conjugate acid of H_2O .

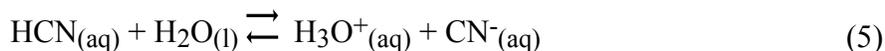
Since equation (2) is an equilibrium reaction, we can write an equilibrium constant expression as shown below

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad (3)$$

The equilibrium constant, K_a , is called the acid dissociation constant. Recall that water is not included in the equilibrium constant expression since it appears in the reaction as the pure liquid. The magnitude of the dissociation constant provides information regarding the degree of dissociation of the acid in water. For example, the K_a values for HF and HCN are 7.2×10^{-4} and 4.0×10^{-10} , respectively. The larger K_a value of HF indicates that the equilibrium reaction between HF and H_2O



lies further to the right than the equilibrium reaction between HCN and H₂O shown below.



In other words, HF dissociates into hydronium ion, H₃O⁺, and its conjugate base, F⁻, to a greater extent than does HCN. If we had a bottle of 0.1 M HF and a bottle of 0.1 M HCN then the hydronium ion concentration would be higher in the bottle of HF than in the bottle of HCN and, therefore, the pH would be lower in the bottle of HF.

Due to the establishment of equilibrium between a weak acid and its conjugate base in an aqueous medium, the pH changes that take place when titrating a weak acid with a strong base are significantly different than the pH changes that take place when titrating a strong acid with a strong base. As a result, the titration curve of a weak acid has a slightly different shape than the titration curve of a strong acid. For example, when a strong acid is titrated with a strong base, the equivalence point is found to occur at pH = 7. However, when a weak acid is titrated with a strong base the equivalence point does not occur at neutral pH. You will also find other significant differences between the two titration curves due to equilibrium reactions.

Let us consider in more detail how pH will change when small amounts of strong base are added to an aqueous solution of a weak acid, HA. Before any strong base is added to the weak acid, the concentration of the hydronium ion can be assumed to originate only from the dissociation of the weak acid.

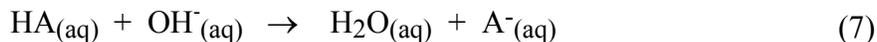


The assumption here is that the amount of hydronium ion resulting from the dissociation of water

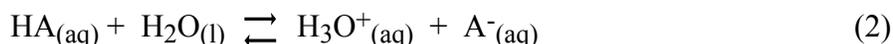


is very small relative to the other sources of hydronium and can be neglected. This is a good assumption since the equilibrium constant, K_w , at 25°C for this reaction is equal to 1.0×10^{-14} . Therefore, the pH then corresponds to the [H₃O⁺] as a result of the dissociation reaction represented by equation (2). Furthermore, for every mole of H₃O⁺ that forms, one mole of A⁻ is produced and one mole of HA dissociates. Therefore, at equilibrium, [H₃O⁺] = [A⁻] and [H₃O⁺] represents the concentration of HA that is lost in the dissociation. Once the initial concentration of HA is known, then the equilibrium concentrations of H₃O⁺, A⁻, and HA can be calculated, as well as, the K_a value of the weak acid from a measured pH value.

As base is added, the OH⁻ ion will react with the major species in solution, HA, to produce more conjugate base, A⁻.



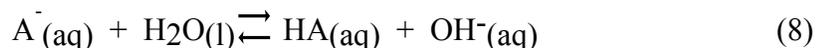
This reaction can be assumed to go to completion followed by the re-establishment of the dissociation equilibrium:



If the equivalence point has not been reached then the number of moles of leftover HA will be equal to the original number of moles HA minus the number of moles of OH⁻. The moles of HA lost in the dissociation reaction, shown by equation (2), is negligible compared to the number of moles of leftover HA. [HA] then is calculated by dividing the number of leftover moles of HA by the total volume of the mixture at this point in the titration. [H₃O⁺] is determined by the number of moles of H₃O⁺ formed in the dissociation reaction and is simply measured by pH. (Again, assuming that any [H₃O⁺] formed from the dissociation of water is negligible.) [A⁻] is equal to the number of moles of A⁻ formed in the strong base reaction, shown by equation (7), divided by the total volume of the mixture. Like HA, the number of moles of A⁻ produced in the dissociation reaction is negligible.

Another point of interest, other than the equivalence point, on a weak acid titration curve is the midpoint. The midpoint occurs when ½ of the original acid, HA, has reacted with all the strong base, OH⁻, added. At the midpoint, the number of moles of the conjugate base, A⁻ is equal to the number of moles of weak acid, HA, remaining in the solution and thus, [HA] = [A⁻]. Applying this to equation (3), we obtain K_a = [H₃O⁺] and taking the negative log of each side the equality is expressed as pH = pK_a. Therefore, at the midpoint, the K_a of the weak acid can be easily calculated from the measured pH level.

At the equivalence point, just enough strong base has been added to completely react with all the weak acid. After reaction, the only species present will be the conjugate base, A⁻. Since A⁻ is a conjugate base, it will accept a proton from water to reform HA and OH⁻ in the equilibrium reaction shown by:



The equilibrium constant expression is given by:

$$K_b = \frac{[HA][OH^{-}]}{[A^{-}]} \quad (9)$$

The equilibrium constant, K_b, is called the **base dissociation constant**. Knowing the original amount of HA placed into the flask, measuring the pH, and making the assumption that the concentration of the OH⁻ is the same as the concentration of HA, you can determine the concentrations of all three of the species in this equilibrium constant expression. K_a of a weak acid the K_b of the corresponding conjugate base are related to each other by the equilibrium constant, K_w.

$$K_w = K_a K_b \quad (10)$$

By subtraction you should be able to calculate the concentration of A⁻ in solution. Finally, using the relationship shown by equation (10), you will be able to re-calculate the value of K_a for the weak acid.

Beyond the equivalence point in the titration the strong base, OH⁻, will be in excess. Here, the excess base determines the pH of the solution. The amount of OH⁻ formed from the equilibrium reaction shown by equation (8) is negligible. You will then plot all the pH measurements made in this experiment against the quantity of strong base added to form a pH titration curve.

In this experiment, you will be titrating the weak acid, acetic acid, with the strong base, sodium hydroxide. After you find the volume of strong base needed to reach the equivalence point of the titration you will use this information to calculate the concentration of the original weak acid solution. You will calculate the acid dissociation constant, K_a , of acetic acid using several measured pH readings along the titration. You will also compare the titration curves of a strong acid titration and weak acid titration.

As pre-laboratory preparation it is critical that you review the ideas presented in Chapter 17 and in Chapter 18 of Petrucci et.al, 8th ed. These chapters address the concepts involved in this experiment.

Safety: Remember to always wear gloves when handling all acids and bases. WEAR YOUR GOGGLES!

Work in pairs on this experiment.

Each student must collect data and submit a separate report.

The actual data analyses and the written reports must be done entirely independently of your lab partner or other students. Make sure that you avoid unauthorized collaboration and plagiarism. All suspected violations of the Code of Academic Conduct will be referred to Student Judicial Affairs.

Experimental Procedure

Preparation for Next Lab

Before starting the Weak Acid Titration experiment and in preparation for next week's Polyprotic Acid experiment, each pair of students needs to dry a sample of solid sodium carbonate.

- 1) Half fill one vial with pure sodium carbonate. You will need approximately 1 g of dry sodium carbonate.
- 2) Place the uncapped vial in a beaker. With a graphite pencil, write your name on the white frosted area of the beaker and place it in the oven. Do NOT use PAPER labels on your vials or beaker. Cover the beaker with a watch glass.
- 3) Dry the sample in the oven for 1.5 hours. Do not adjust the temperature on the oven. The temperature on the oven has been preset and will heat to the correct temperature when the door remains closed.
- 4) After removing your sample from the oven, let it cool until it is warm but safe to handle.
- 5) After the sample has cooled, carefully place the beaker containing the uncapped vial in the desiccator until needed. Be careful not to touch the vial with your fingers.

Make sure that you label the vial!

Part I. Preparing the Acetic Acid Solution

In this step of the experiment, you will prepare 200 ml of approximately 0.1 M acetic acid solution by diluting the stock solution of 6 M acetic acid. You will need to calculate the volume of stock solution required in this dilution. Mix well

Part II. Weak Acid Strong Base Titration Curve

This experiment requires the use of a pH meter to measure the pH of various solutions. The pH meter and the accompanying electrode are both very expensive and fragile. Treat both pieces of equipment with great care. Follow the directions provided very carefully. When rinsing the electrode use a light stream of deionized water. Be careful of the electrode when adding strong

base or when stirring the solution. After completing the experiment, STORE THE ELECTRODE IN THE STORAGE SOLUTION provided.

Titration Set up

1. Find your 1L bottle of your standardized NaOH from the previous experiment, "Strong Acid - Strong Base Titration." Before opening the bottle of NaOH, carefully, invert it several times to ensure that your solution is uniform. Take a 50 ml buret and condition it with your standardized NaOH solution.
2. After conditioning, fill the buret to above the zero mark, place buret in clamp, and dispel any air bubbles from the stopcock. Record the initial buret reading to two decimal places, i.e. 1.24 mL. Remember when filling a buret to check that the stopcock is closed. While holding the buret at a safe level, use a funnel when pouring in your sodium hydroxide solution.
3. Condition a second buret with your dilute acetic acid solution. Fill the buret with your dilute acetic acid solution. Record the initial buret reading to two decimal places, i.e. 0.58 mL.
4. Dispense into a 150 mL beaker approximately 30.00 mL of the dilute acetic acid solution. Record the precise volume to the nearest 0.02 ml. To this solution, add 3-5 drops of thymolphthalein indicator and without splashing carefully place a clean magnetic stir bar into the beaker.
5. Standardize the pH meter nearest your work area using the three buffer solutions at pH 4.00, pH 7.00, and pH 10.00 following the specific directions for use of the pH meters that are provided in the laboratory. Be sure to use your wash bottle to rinse off the pH electrode into a waste beaker before and after using it in each of the buffer solutions. Wipe the end of the electrode with a Kimwipe before placing it in a new solution. Always keep the pH electrode wet when not in use. For long-term storage place the electrode in a beaker of tap water or a container of pH 7.00 buffer solution.
6. Set up the stir plate underneath the buret containing the sodium hydroxide and place the beaker containing your dilute acetic acid solution onto the stir plate. Turn the stir knob to a low setting until the magnetic field catches the stir bar and begins to spin it. Be sure to turn the correct knob. These stir plates also have a knob for heating. Gradually increase the speed of the stir bar until it is smoothly stirring the solution. You may need to center the beaker on the stir plate in order to achieve smooth stirring.
7. Using your extension clamp to hold the pH electrode near the edge of the beaker so that it is submersed in the acetic acid solution but not touching the bottom of the beaker or interfering with the stir bar. Lower the buret so that the tip is just below the opening of the beaker.
8. Before adding any NaOH, measure and record the pH of the dilute acetic acid solution.

The Titration

9. First, you will do a quick titration to find the approximate endpoint. Carefully add approximately 1 mL of NaOH to the beaker. Record the buret reading to two decimal places, i.e. 2.34 mL. Allow the solution to mix and equilibrate. After the pH meter has stabilized record the pH of this mixture to two decimal places, i.e. 2.34. Continue adding NaOH in 1 mL increments to the acid solution, recording the pH of the solution after each addition. When the solution starts to turn faint blue make a note of the color change alongside the volume of sodium hydroxide added. Continue adding 1 mL increments of NaOH, recording the buret reading and pH after each increment until you reach a $\text{pH} > 11$. Do not use your wash bottle to rinse down the sides of the beaker at any time during this titration, as the volume of water added during the wash would invalidate the pH readings. The only volume changes that may take place must come from added HCl solution.
10. Before doing your 2nd titration, you will need to estimate the equivalence point and the midpoint by graphing pH vs. volume of NaOH added. Convert your buret readings to volumes of NaOH added. In your notebook, graph a titration curve by plotting pH level on the ordinate (y-axis) and the volume of NaOH added on the abscissa (x-axis). Find the area of the graph where the change in pH is the greatest, in other words, where the slope is the highest. The equivalence point is in this region. Consider the volumes of NaOH that bracket this region and estimate the volume of NaOH needed to reach the equivalence point. Also, estimate the volume of NaOH needed to reach the midpoint of the titration.
11. The next titration will be performed more precisely to accurately determine the midpoint and the equivalence point. Refill your burets with the appropriate solutions and prepare another sample to be titrated following the same set up procedures as with the first titration. Record the initial buret reading.
12. After recording the pH of the acetic acid solution, begin the titration by adding 1 mL increments of NaOH until you are within 2 mL of the midpoint. After each addition, allow the solution to equilibrate and the pH to stabilize. Record the pH after each 1 mL addition.
13. Once you are within 2 mL of the estimated midpoint, add your NaOH 2 drops at a time until you are 2 mL beyond the midpoint. After each addition, allow the solution to equilibrate and the pH to stabilize. Record the buret reading and the pH after each 2-drop addition.
14. Return to adding 1 mL increments of NaOH until you are within 2 mL of the endpoint. After each addition, allow the solution to equilibrate and the pH to stabilize. Record the buret reading and the pH after each 1 mL addition.

15. When you are within 2 mL of the estimated endpoint, add your NaOH 2 drops at a time until you are 2 mL beyond the endpoint. After each addition, allow the solution to equilibrate and the pH to stabilize. Record the buret reading and the pH after each 2-drop addition.
16. Return to adding 1 mL increments of NaOH until pH > 11. After each addition, allow the solution to equilibrate and the pH to stabilize. Record the buret reading and the pH after each 1 mL addition.
17. Repeat Titration procedure, steps 11- 16, at least one more time.

Clean-Up

Pour the contents of the beaker and the remaining solutions in the buret down the drain, rinsing with copious amounts of water. Carefully clean the buret containing the NaOH by rinsing it with a few ml of acetic acid followed by several rinsings with deionized water. Rinse all other glassware. Pour down the drain with copious amounts of water, any remaining NaOH solution that is in your 1L bottle. You should still have your 1L bottle of standardized HCl in your locker. Save this solution for the Polyprotic Acid Experiment.

Data Analysis

Part I

1. What volume of 6 M HC₂H₃O₂ stock solution did you use to prepare the 1L of 0.1 M HC₂H₃O₂? Show how you calculated this volume.

Part II

2. How many trials did you perform to determine the titration curve for the neutralization of HC₂H₃O₂ by NaOH?
3. Using a spreadsheet program such as Excel, enter the volume of NaOH added and corresponding pH levels and plot the pH level on the ordinate (y-axis) and the volume of NaOH added on the abscissa (x-axis) to obtain a titration curve for each set of trial data. Use these plots to estimate the position of the equivalence point (that volume of NaOH which is midway between the two nearly linear asymptotic regions at low pH and at high pH). What is your best estimate of the volume of NaOH required to reach the equivalence point for each of your titration curves?
4. Compare and contrast the shape and trends of this titration curve to the strong acid-strong base titration curve. At what pH, does the equivalence point occur for each of the graphs? How do the slopes of the titration curves compare?
5. As instructed in questions 8 & 9 of the "Titrating a Strong Acid with a Strong Base" experiment calculate the volumes and the forward difference approximations for the first and second derivatives using each set of trial data. Graph the approximations to the first and second derivatives vs. NaOH volumes as you did in the previous laboratory report. **Print copies of all your graphs and turn them in to your teaching assistant. Make sure your name is on each of the graph. Clearly, title and label the vertical and horizontal axes.**

6. Using the combined representations of the derivative graphs developed in questions 4 and 5, estimate the volume of NaOH required to reach the equivalence point for each of your trials. You should be able to make this estimate to within 0.02 mL i.e. 32.46 mL.
7. Using the initial volume of acetic acid, the volume of NaOH at the equivalence point and the standardized molarity of your NaOH, calculate the molarity of acetic acid you obtained in each of your trials. Then calculate the average value of the molarity of your acetic acid solution and use this value in all subsequent calculations where the molarity of the acetic acid solution is required.
8. Average the value of the initial pH of your acetic acid solutions before any NaOH was added, and calculate the K_a of acetic acid based on your calculated average molarity and the average pH of the acetic acid solution before any sodium hydroxide was added.
9. Find the pH of the midpoint for each of the trials using half the volume of NaOH required to reach the equivalence point for that trial. Use the sum of the initial volume and the volume of NaOH to reach the midpoint as the total solution volume at the midpoint. Combine these data with the pH at the midpoint to calculate K_a for each trial.
10. Calculate the average K_a of acetic acid based on the pH at the midpoint from each of your trials.
11. For each trial, calculate the K_a of acetic acid based on your calculated average molarity the initial volume of acetic acid, the volume of NaOH required to reach the equivalence point, and the pH of your acetic acid solution at the equivalence point. Then calculate the average value of K_a from the equivalence point determinations.
12. Compare the rate of change of pH vs. volume of NaOH at the midpoint to the rate of change vs. volume of NaOH at the equivalence point on the weak acid titration curve. The rate of change of pH vs. volume is $(\text{pH}(i) - \text{pH}(i-1))/(\text{V}(i) - \text{V}(i-1))$. Which is larger? Which pH has the greater uncertainty, the equivalence point pH or the midpoint pH?
13. Calculate the concentrations of the acetic acid and the acetate ion at the midpoint.
14. Calculate the concentrations of the acetic acid and the acetate ion after 25 mL of NaOH is added.
15. At what volume of NaOH did the indicator change color? Does this agree with the volume of NaOH needed to reach the equivalence point? What does this suggest to you about the selection of an indicator for an acid-base titration?

16. Which solution would have a higher pH, 0.1 M HBr or 0.1 M HC₂H₃O₂? Explain.

Conclusion Take a moment to reflect on the standardization of acetic acid and the titration curves, and then compose a summary paragraph that describes today's experiment and your new understanding of weak-acid titration reactions. How does the weak acid titration curve differ from the strong-acid titration curve?