14. INVESTIGATION OF ACID-BASE TITRATIONS

Introduction

Titration curves have distinctive shapes that change predictably when weak acids are substituted for strong acids. One simple explanation for this is that their pHs differ based on their different chemistry. However, factors, other than acid strength, also contribute to differences in the shapes of titration curves. In this lab, you will examine the shapes of titration curves of strong and weak acids then apply that knowledge to understanding what factors influence the shape of a curve. Moreover, you will investigate the pH titration curves of mono- and polyprotic weak acids and relate this to their K_a values.

Concepts

- Titration
- Strong and weak acids
- Mono- and polyprotic acids
- Equivalence point
- K_a expressions
- pH
- Neutralization reactions

Background

Titration is a simple analytical method that uses volume measurements to quantitate the amount of a chemical species in solution. In a typical acid-base titration, the method is used to determine how much acid or base is present in an unknown. The reaction between the acid and base is a neutralization whose net ionic equation yields water as a product. It is stoichiometric and it is this proportionality that is key in quantifying the concentration of an unknown species relative to a known standard. For example, a solution of hydrochloric acid of unknown concentration (analyte) can be titrated with a standardized solution of sodium hydroxide (titrant). At the equivalence point, the point at which stoichiometric amounts of the acid and base have combined, the exact volume of the titrant needed to react completely with the analyte is used to calculate the concentration of the unknown species.

Titration curves of strong acids differ from those of weak acids. The differences stem from a number of factors. Perhaps the most obvious difference between strong and weak acids is their pH. Due to the partial ionization of weak acids, their intrinsic pH is higher than that of strong acids. Factors other than acid strength, also influence the shape of titration curves. For example, does acid concentration influence the shape of a titration curve? What happens if an acid is polyprotic (has more than one ionizable proton)?

K_a is the symbol for the equilibrium constant for the ionization of an acid. The following equation describes the ionization of an acid:

$$HA + H2O \rightleftharpoons H3O+ + A–$$

When equilibrium exists, the acid dissociation constant can be written as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The value of K_a is an indication of the extent to which an acid dissociates. Strong acids dissociate nearly completely. Weak acids reach equilibrium, where the fraction that has dissociated remains constant at a given temperature. The numerical value of the equilibrium constant is unique to the acid and can be used to identify an unknown acid.

The half equivalence point is a very useful point in determining the K_a of an acid. At this point, the $[HA] = [A^-]$ so $K_a = [H_3O^+]$. Taking the negative log of both sides, the pK_a equals the pH.

Polyprotic acids are acids that have more than one acidic proton. Among organic molecules, those considered to be polyprotic have more than one carboxylic group (COOH).

$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]}$$

$$K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]}$$

If the K_a values for a polyprotic acid are distinct enough, then two equivalence points appear in a titration curve. But if the K_a values are too close, the polyprotic acid will not show titration curves with multiple equivalence points.

For example, fumaric acid has two acidic hydrogen atoms with the following K_a values:

$$K_{a1} = 9.33 \times 10^{-4}, \quad pK_{a1} = 3.03$$

$$K_{a2} = 3.63 \times 10^{-5}, \quad pK_{a2} = 4.44$$

where “1” and “2” refer to the first and second acidic hydrogen ions.

When fumaric acid is titrated, both acidic protons detach at nearly the same time and the two equivalence points are not easily detected. Usually the equivalence points show up as a single equivalence point somewhere between the two values.

Pre-Lab Questions

1. Write a balanced chemical equation and net ionic equation for the reaction of a strong acid, HCl, with a strong base, NaOH.

2. Write a balanced chemical equation and net ionic equation for the reaction of a weak acid, CH_3COOH with a strong base, NaOH.

3. Calculate the volume of 0.25 M NaOH needed to completely react with 30.0 mL of 0.15 M HCl.

Materials and Equipment

Use the following materials to complete the initial investigation. For conducting an experiment of your own design, check with your teacher to see what materials and equipment are available.

- Data collection system
- Wireless pH sensor
- Wireless drop counter
- Titration syringe assembly[2]
- Beaker, 150 mL
- Beakers, 250-mL
- Volumetric pipet, 25-mL
- Pipet bulb
- Magnetic stir plate
- Ring stand
- Wash bottle with distilled water
- 0.50 M Sodium hydroxide ($NaOH$), 160 mL[1]
- 0.10 M Sodium hydroxide ($NaOH$), 260 mL[1]
- 0.10 M Hydrochloric acid (HCl), 20 mL[1]
- 0.05 M Hydrochloric acid (HCl), 20 mL[1]
- 0.025 M Hydrochloric acid (HCl), 20 mL[1]
- 0.10 M Acetic acid (CH_3COOH), 20 mL[1]
- 1.0 M Acetic acid (CH_3COOH), 20 mL[1]
- 0.05 M Maleic acid ($C_3H_4O_4$), 50 mL[1]
- Phenolphthalein indicator solution
-

[1]To formulate these solutions, refer to the Lab Preparation section

[2] Included with Wireless drop counter

Safety

Follow these important safety precautions in addition to your regular classroom procedures:

- Wear safety goggles and gloves at all times. This lab uses strong acids and bases.
- Hydrochloric acid is corrosive. If you come in contact with it, flush the area with plenty of water. It can cause severe tissue burns.
- Sodium hydroxide is caustic and should be handled with special care.
- In case of contact with your skin, wash off the acid and base solutions with a large amount of water.
- Wash hands thoroughly with soap and water before leaving laboratory.
- Review chemical handling and disposal instructions as directed by Material Safety Data Sheet.

Disposal

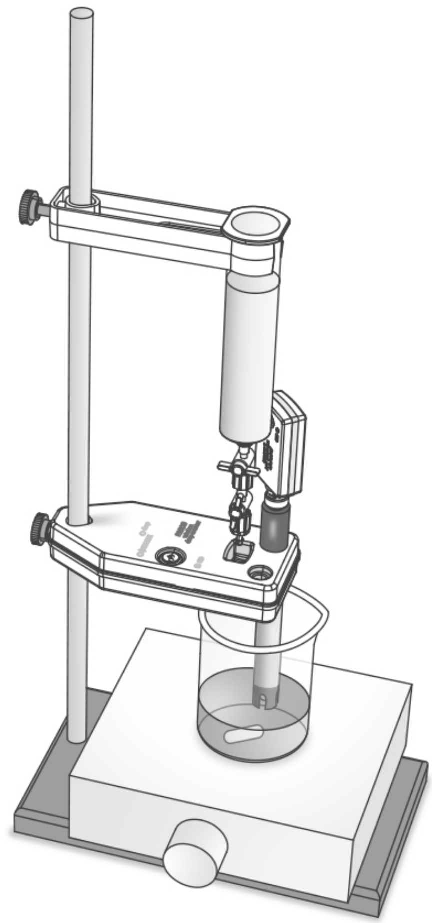
If your drain system is connected to a sanitary sewer system, the following instructions apply. Acid and base solutions may be rinsed down the drain with an excess of water.

Initial Investigation

Titration of a strong acid with a strong base

1. Start a new experiment on your Chromebook, computer or mobile device.

2. Connect pH sensor and drop counter to the data collection system. Open lab file *14 Acid-Base Titration* or create a graph of pH vs. Volume (mL).



3. Attach the drop dispenser syringe using instrument clamp.

4. Rinse the drop dispenser syringe:

   a. Place a 250-mL beaker under the drop dispenser and open both stopcocks.

   b. Rinse the drop dispenser syringe and stopcock three times with approximately 20 mL of distilled water. This will remove any residue.

   c. Rinse the drop dispenser three times with 20 mL of the 0.10 M NaOH. This removes remaining water that would dilute the NaOH solution.

   d. Discard the rinse solution as directed by your teacher.

5. Calibrate the drop counter and pH sensor.

   NOTE: Do not disconnect the drop counter from the data collection system or it will need to be calibrated again.

6. Assemble the rest of the apparatus using the following steps and the illustration as a guide.

   a. Position the magnetic stirrer on the base of the ring stand.

   b. Position the drop counter over the magnetic stirrer.

   c. Place the pH sensor through a large slot in the drop counter.

7. Display the pH on the *y*-axis of a graph and fluid volume on the *x*-axis.

8. Use the graduated pipet to transfer 20.00 mL of 0.10 M HCl and 30.0 mL of distilled water to a 150-mL beaker and set the beaker on the magnetic stirrer.

9. Add two drops of phenolphthalein indicator solution to the solution in the beaker.

10. Turn on the magnetic stirrer at a slow and steady rate.

11. Start recording data.

12. Turn the drop dispenser stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

NOTE: The top valve controls the flow rate and the bottom valve turns the flow on and off.

13. Record the approximate pH where the phenolphthalein turns from clear to pink and the volume of titrant used. Do not stop the titration at this point. Continue the titration until the pH curve flattens, somewhere between pH 10 and pH 14.

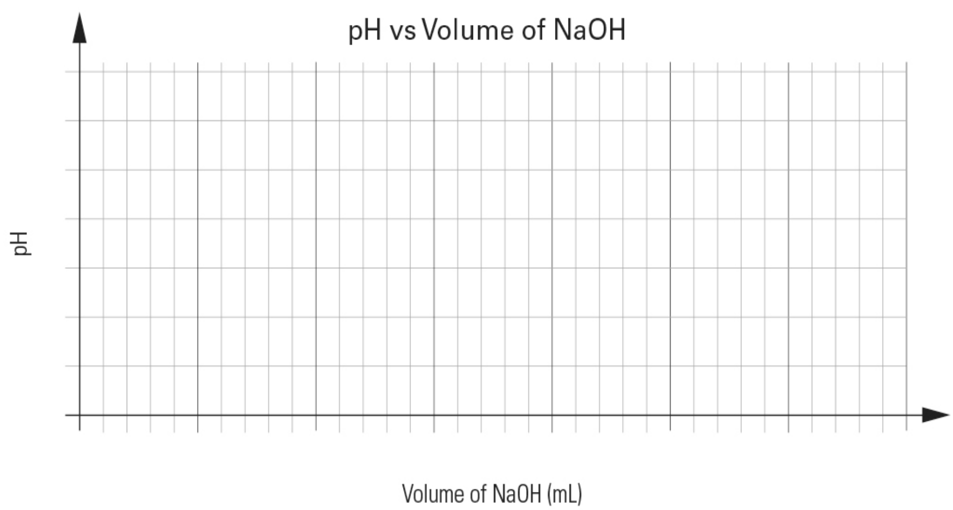
14. Stop recording data.

15. Save your experiment and dispose of the contents of the beaker according to your teacher's instructions.

16. Graph pH versus volume of NaOH added in the space provided below. In the Table 1, record the concentration of base, acid and the volume of acid used.

Table 1: Titration of strong acid with strong base

Titration Information	
Parameter	**Value**
Concentration of NaOH (M)	
Concentration of HCl (M)	
Volume of HCl sample (mL)	
Volume of titrant (NaOH) added when indictor changed color (mL)	
pH of indicator color change	



17. Assuming the reaction between HCl and NaOH goes to completion, because they are a strong acid and base, calculate the volume of 0.10 M NaOH needed to completely neutralize the acid in the beaker.

18. The point in the reaction at which the number of moles of base added equals the number of moles of acid originally present in the sample is called the *equivalence point*. What volume of 0.10 M NaOH needs to be added to your acid to reach the equivalence point?

19. Describe and label the equivalence point on the graph.

20. For a strong acid–strong base titration, the pH at the equivalence point should be 7.

a. Consider the products of the neutralization reaction and explain why an equivalence point pH of 7 makes sense.

b. If the equivalence point pH of your graph is not close to 7, propose some sources of error that may have skewed your data.

❷ 21. The endpoint of a titration occurs when the indicator solution changes colors. Compare the pH when the indicator changed color during your titration and the pH of the equivalence point on your graph. Describe any similarities.

Advanced Investigation

Titration of a weak acid with a strong base

1. Discard contents of the syringe reservoir and rinse the drop dispenser syringe reservoir three times with small volumes of 0.5 M NaOH. Refill the reservoir with about 60 mL of 0.5 M NaOH. This is your titrant.

2. Set up titration apparatus as detailed in the Initial Investigation. Open page 2 of the lab file or create a new graph of pH vs. Volume (mL).

3. Measure 10.0 mL of a 1.00 M acetic acid solution into the 150-mL beaker and add 40.0 mL distilled water.

4. Record concentration of the base and weak acid and the volume of weak acid used in Table 2 below.

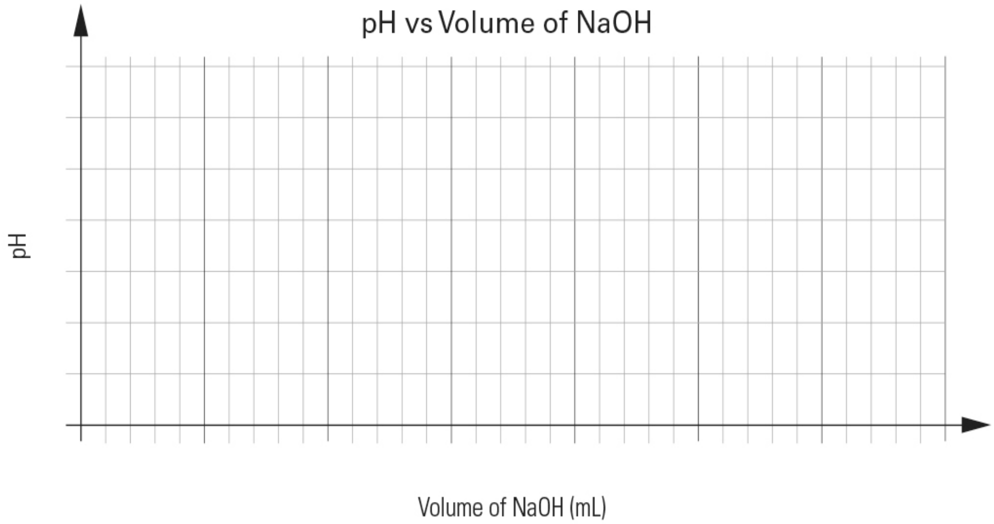
5. As you lower the pH electrode into the analyte, ensure that the tip of the electrode is completely immersed in the solution.

6. Begin titration and data recording as detailed in the Initial Activity.

7. Record graph of pH versus NaOH volume in the space provided below.

Table 2: Titration of a weak acid with strong base

Titration Information	
Parameter	**Value**
Concentration of NaOH used (M)	
Concentration of CH_3COOH used (M)	
Volume of weak acid sample (mL)	



8. Write the net ionic equation for the neutralization being performed in the titration.

9. Answer the questions below to understand what information can be gained from a pH titration curve as the sodium hydroxide is added.

   a. Explain why the pH of the solution starts below 7.

   b. What is happening to the pH of the weak acid solution as sodium hydroxide is added to the beaker? Explain what process is changing the pH.

   c. The *equivalence point* represents the point in the titration where a *stoichiometrically equivalent* amount of base has been added to the acid. Using your graph, at what volume of titrant does this occur?

   d. Describe the change in pH at or around the equivalence point.

   e. Is the solution acidic, basic, or neutral at the equivalence point?

   f. Using the net ionic equation for the reaction, identify the species present in the beaker at the equivalence point. Which species in the solution is responsible for the pH? Write a chemical reaction for that species reacting with water to support your answer.

10. The half-equivalence point is the volume of titrant halfway between the start of the titration and the equivalence point. Answer the questions below to determine the half-equivalence point on your titration curve and the information it provides.

   a. Determine the volume of titrant at the half-equivalence point.

   b. According to the titration curve, what is the pH at the half-equivalence point?

   c. Calculate the concentration of hydronium ion, $[H_3O^+]$, at the half-equivalence point.

   d. Calculate the number of moles of weak acid HA present before the titration and the number of moles that remain at the half-equivalence point.

   e. Based on the balanced equation $CH_3COOH + OH^- \rightleftharpoons H_2O + CH_3COO^-$, calculate the number of moles of conjugate base A^- that have formed at the half-equivalence point.

f. How do the number of moles of HA and the number of moles of A^- compare at the half-equivalence point? Since the HA and A^- are in the same solution, how do the concentrations of HA and A^- compare at half equivalence point?

g. Write the acid ionization expression for a weak acid, HA.

h. Based on the relationship between the [HA] and [A^-] values, how can the acid ionization constant be simplified at the half-equivalence point?

i. How do the pK_a of the acid and the pH of the half-equivalence point compare?

j. Explain why the half-equivalence point is the most useful point on the titration curve for determining the K_a of an unknown acid.

Titration of a weak polyprotic acid with a strong base

1. Set up the titration as detailed in the Initial Investigation. Open lab file to page 3 or create a new graph of pH vs. Volume (mL).

2. Refill the drop dispenser syringe reservoir with the titrant, 0.5 M NaOH, as necessary.

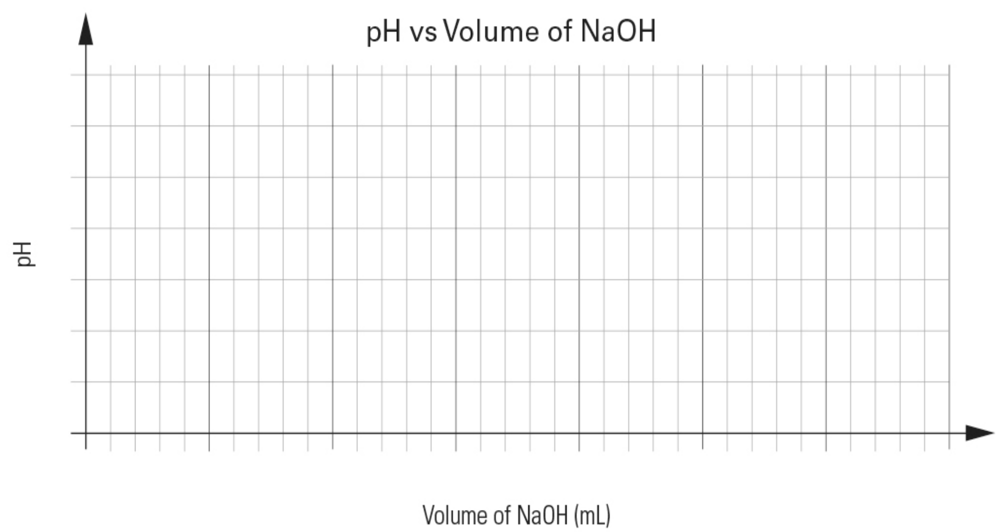
3. The analyte solution for this titration will be 50.00 mL 0.05 M maleic acid.

4. Add distilled water to the analyte as needed to completely immerse the pH electrode tip.

5. Run the titration protocol and graph pH versus volume of NaOH added in the space provided below.

Table 3: Titration of a polyprotic acid with a strong base

Titration Information	
Parameter	**Value**
Concentration of NaOH used (M)	
Concentration of $C_3H_4O_4$ used (M)	
Volume of weak acid sample (mL)	



6. Below is the structural formula for maleic acid. Circle the hydrogen atoms that can ionize.

7. What features are different on the graph of a weak acid titration compared to the graph of a strong acid titration?

8. How is the structure of maleic acid related to the titration curve?

9. Write the equation for the reaction of each hydrogen atom of maleic acid that ionizes with sodium hydroxide.

10. What volume of NaOH is required to reach each of the equivalence points?

11. Calculate the volume of titrant added to reach the half-equivalence point of each equivalence points.

12. Use the graph to determine the pH and pK_a at the half-equivalence points.

13. Record the literature values of the pK_a for maleic acid.

14. What is the percentage of error between the literature values and the values you determined from the titration?

Extended Inquiry Investigation

Comparison of the acid-neutralizing capacity of different commercial antacids

Design an experiment to determine the relative acid-neutralizing capacity of several commercial antacid formulations. The protocol will require standardization of a solution of hydrochloric acid using 0.1 M NaOH as detailed in the Initial Investigation section. Student lab groups will work with different commercial formulations. Antacids must be ground and suspended in water before titration with standardized acid. Class data will be shared to determine which product has the best acid-neutralizing capacity by mass.

Synthesis Questions

1. If you analyze (using titration) a sulfuric acid (H_2SO_4) solution with approximately the same concentration and volume as the HCl solution, how would the volume of NaOH consumed be different? (Hint: H_2SO_4 yields two H^+ ions when it dissociates.)

2. How would your results be different if you pipet some of the NaOH standard solution into a beaker and titrate with the unknown HCl solution?

AP® Chemistry Review Questions

$$\mathbf{CH_3CH_2COOH(aq) + H_2O \Leftrightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)}$$

Propanoic acid (CH_3CH_2COOH) is a carboxylic acid that reacts with water according to the equation above. At 25 °C, the pH of a 50.0 mL sample of 0.20 M CH_3CH_2COOH is 2.79.

1. Determine the value of K_a for propanoic acid at 25 °C.

2. In a titration experiment, 25.00 mL of propanoic acid of unknown concentration are titrated with a 0.173 M NaOH solution. Using a color indicator, the volume of NaOH needed to reach end point is determined to be 20.52 mL. Calculate the concentration of a propanoic acid solution.