14. WEAK ACID TITRATION

Initial Question

Weak acids have a slightly different chemistry than strong acids. If the pH of a strong acid solution and a weak acid solution of equal concentration were analyzed, the weaker acid would have a higher pH. This is due to the partial ionization of the weak acid. However, if the weak acid is neutralized by a strong base, the weak acid is forced to ionize completely.

What information can you derive from a pH titration curve of a weak acid?

Materials and Equipment

Model1, Model 2, and Applying Your Knowledge

- Data collection system
- pH sensor
- Drop counter
- Drop dispenser:
  Syringe, 60-mL
  Stopcock (2)
  Drop tip
- Beaker, glass, 150-mL
- Beaker, 250-mL
- Mohr pipet, 25-mL
- Magnetic stirrer (stir plate)
- Micro stir bar
- Pipet pump
- Multi clamp
- Ring stand
- Three-finger clamp
- 0.50 M Sodium hydroxide (NaOH), 160 mL
- Distilled water, 260 mL
- Wash bottle
- Materials for drop counter and pH sensor calibration (refer to Appendix A)

Model 1

- 1.0 M Acetic acid (CH_3COOH), 20 mL

Model 2

- 0.05 M Maleic Acid ($C_3H_4O_4$), 50mL

Applying Your Knowledge

- Aspirin

Safety

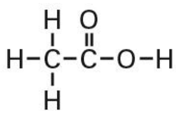
Add these important safety precautions to your normal laboratory procedures:

- Sodium hydroxide is caustic and should be handled with special care. In case of contact with your skin, wash off the sodium hydroxide with a large amount of water.

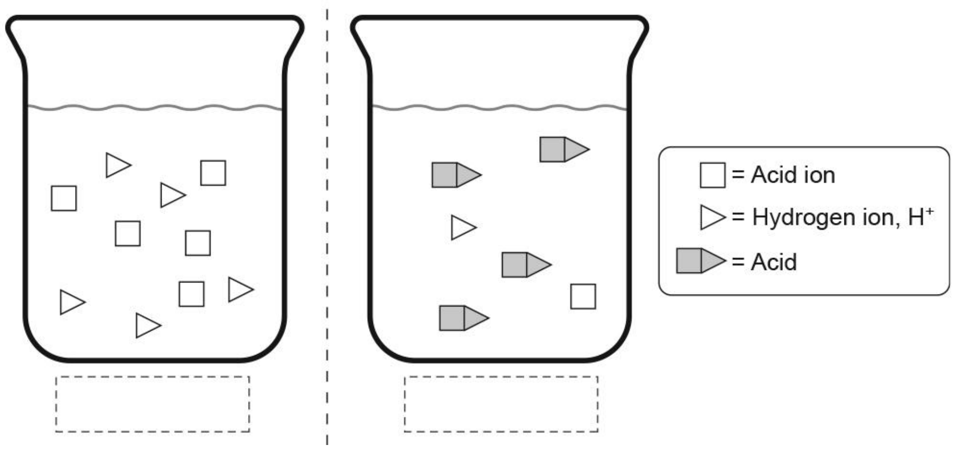
Getting Your Brain in Gear

1. Compare the ionization of a strong acid to that of a weak acid.

2. Acetic acid is a weak monoprotic acid. Circle the ionizable hydrogen on the formula below.



3. Analyze the following particulate-level representations of two acidic solutions. Label one beaker as the strong acid and the other as a weak acid. Explain your reasoning.



4. Write the K_a expression for the equation: $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

5. Will the K_a of a weak acid be greater or less that the K_a of a strong acid? Why?

MODEL 1

Building Model 1 – pH Titration of a Weak Acid

1. Start a new experiment on the data collection system.

2. If 0.50 M sodium hydroxide solution is the titrant and the weak acid, HA, is the analyte, which solution should go into the buret (or syringe) and which should go into the beaker?

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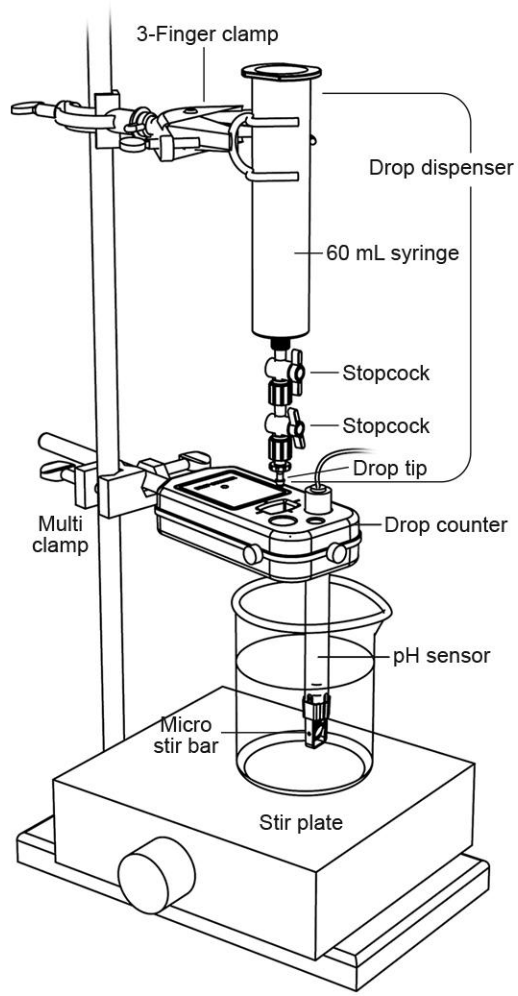


3. Use the multi-clamp to attach the drop counter to the ring stand. Use the illustration as a guide.

4. Use the three-finger clamp to attach the drop dispenser to the ring stand.

5. 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 0.5 M NaOH. This removes remaining water that would dilute the NaOH solution.

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

6. See Appendix A to set up and calibrate the drop counter and pH sensor and then set up the remaining equipment as illustrated.

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

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 10.00 mL of 1.00 M acetic acid solution to a 150-mL beaker and set the beaker on the magnetic stirrer as in the picture. Rinse the pipet with distilled water.

9. Add distilled water to the acid in the 150-mL beaker until the glass tip of the pH electrode is submerged.

10. In order for the tip of the pH electrode to be covered, distilled water must be added to the solution in the beaker.

a. Does adding water to the analyte change the molarity of the sample?

b. Does adding water to the analyte change the number of moles of acid in the sample?

c. Will adding water to the analyte affect the volume of titrant needed to reach the equivalence point for the titration? Explain your answer.

11. Turn on the magnetic stirrer at a slow and steady rate.
12. Start recording data.
13. Turn the drop dispenser stopcock carefully, allowing the titrant to drip slowly at a rate of 1 to 2 drops per second into the solution.

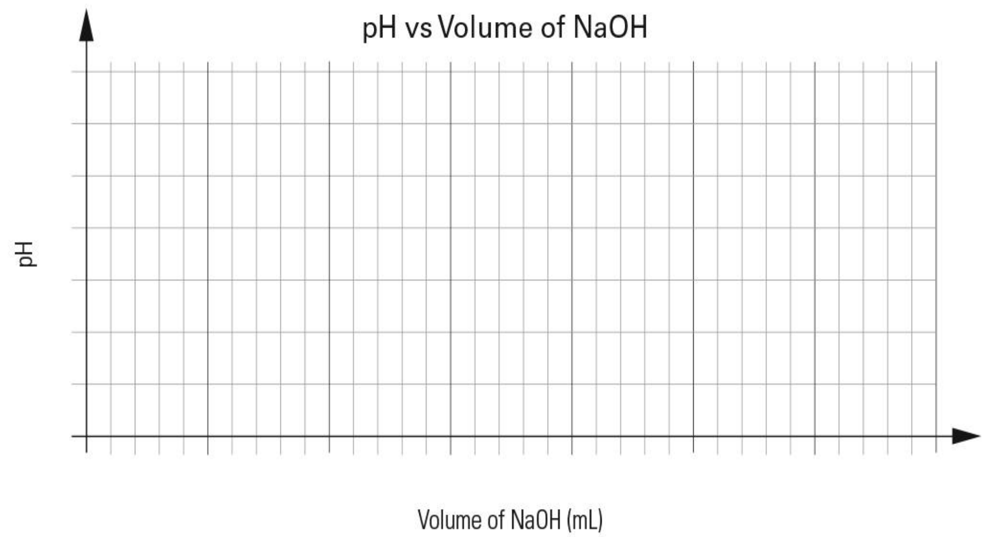
    NOTE: The top valve controls the flow rate and the bottom valve turns the flow on and off.
14. Continue the titration until the pH curve flattens, at around pH 12–14.
15. Stop recording data.
16. Save your experiment and dispose of the contents of the beaker according to your teacher's instructions.
17. Sketch or attach a copy of your graph of pH versus volume of NaOH added to Model 1. In the Model 1 Data Table, record the concentration of the base and the weak acid, and the volume of the weak acid used.

Model 1 – pH Titration of a Weak Acid

Table 1: Model 1 Data Table—Determining the equivalence point

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

Model 1 Graph



Analyzing Model 1 – pH Titration of a Weak Acid

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

19. 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.

20. 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?

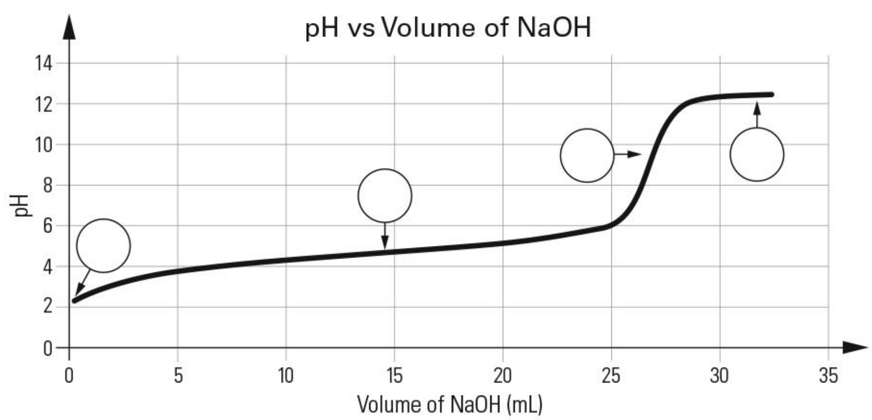
g. Write the acid ionization expression for a weak acid, HA.

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.

21. Label the pH titration graph below with the letters corresponding to the following items:



a. The point in the titration where the pH is determined by the concentration and strength of the weak acid sample.

b. The point in the titration where the pH is determined by excess titrant.

c. The point in the titration where the pH is determined by the concentration and strength of the conjugate base of the weak acid.

d. The point in the titration where the pH is equal to the pK_a.

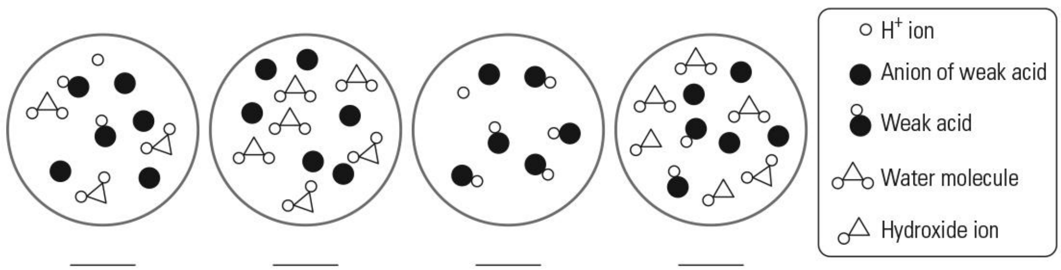
22. Label the particulate view pictures below with the letters corresponding to the following items:

a. Before the titration

b. Halfway to the equivalence point

c. At the equivalence point

d. After the equivalence point



23. An alternate way of doing the titration in Model 1 would be to use an acid–base indicator to determine the equivalence point. Ideally, the end point of the titration, the point at which an added indicator changes color, should occur at or near the equivalence point of the titration—the point where the acid has completely reacted with the base.

a. Using the pH titration curve that you created in Model 1, at what volume would each indicator below begin to change colors?

Table 2: Using indicators to detect the equivalence point

Indicator	Color Change	pH Where Change Occurs	Volume When Change Begins
Methyl red	Red to Yellow	4.2 to 6.3	
Bromothymol blue	Yellow to Blue	6.0 to 7.6	
Phenolphthalein	Clear to Pink	8.0 to 9.6	

b. Which indicator in the table above would have best identified the equivalence point of the titration in Model 1?

MODEL 2

Building Model 2 – pH Titration of a Weak Polyprotic Acid

NOTE: If the drop counter has been disconnected from the data collection system, it will need to be calibrated (see Appendix A).

1. Set up the titration as you did in Model 1. Use the graduated pipet to transfer 50.00 mL of 0.05 M maleic acid solution to a 150-mL beaker and set the beaker on the magnetic stirrer.
2. Add distilled water to the acid in the 150-mL beaker until the glass tip of the pH electrode is submerged.
3. Turn on the magnetic stirrer at a slow and steady rate.
4. Start recording data.
5. Turn the drop dispenser stopcock carefully, allowing the titrant to drip slowly at a rate of 1 to 2 drops per second into the solution.
6. Continue the titration until the pH curve flattens, at around pH 12–14.
7. Stop recording data.
8. Save your experiment and dispose of the contents of the beaker according to your teacher's instructions.
9. Sketch or attach a copy of your Model 2 graph of pH versus volume of NaOH added. In the Model 2 Data Table, record the concentration of the base and the weak acid, and the volume of the weak acid used.

Model 2 – pH Titration of a Weak Polyprotic Acid

Model 2 Graph

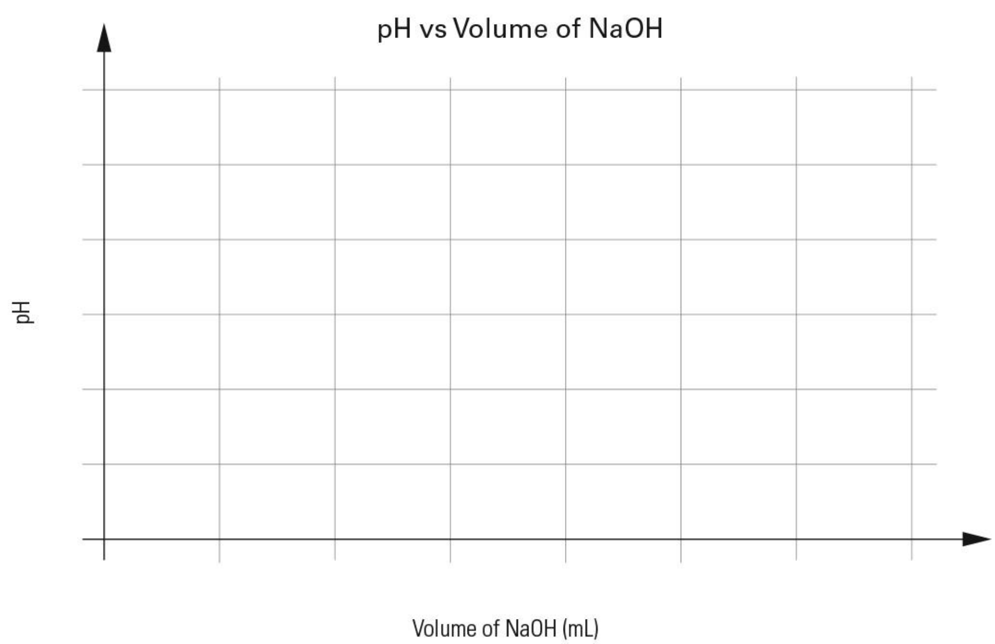
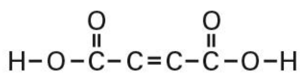


Table 3: Model 2 Data Table—Determining the equivalence point

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

Analyzing Model 2 – pH Titration of a Weak Polyprotic Acid

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



11. What features are different on the Model 2 graph as compared to the graph in Model 1?

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

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

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

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

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

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

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

Connecting to Theory

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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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.

Multiprotic acids are acids that have more than one acidic proton. Among organic molecules, those considered to be multiprotic 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 multiprotic acid are distinct enough, then two equivalence points appear in a titration curve. But if the K_a values are too close, the multiprotic 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.

Applying Your Knowledge – Determine the Amount of Acetylsalicylic acid in Aspirin

You will be given one solid aspirin tablet. Use titration to see if you can identify the acid in aspirin as acetylsalicylic acid based on the K_a value(s) and to determine if the amount of acetylsalicylic acid in the tablet matches the amount on the manufacturer's label.

NOTE: Acetylsalicylic acid is a weak acid and doesn't dissolve well. Therefore, for the titration, use a piece of the aspirin of approximately 0.1 g.

Before you perform the experiment, research and determine the following:

- How much acetylsalicylic acid is reported to be in one aspirin tablet, according to the bottle?

- What is the percentage of acetylsalicylic acid in your aspirin?

- Being a weak acid, acetylsalicylic acid can be difficult to dissolve. Use approximately 0.1 g of aspirin for the titration. From the mass you measured, calculate the amount of acetylsalicylic acid in your sample.

- List observations that indicate the aspirin has fully dissolved.

- What is the molecular formula and molar mass of acetylsalicylic acid?

- Is acetylsalicylic acid monoprotic or polyprotic?

- What are the equation(s) for the reaction(s) between acetylsalicylic acid and sodium hydroxide?

Based on the literature value(s) of K_a for acetylsalicylic acid, how many equivalence points will you expect to see, and what are the value(s)?

After you have performed the experiment and collected your data, determine the percentage of error for K_a. Also determine the percentage difference in the reported mass of acetylsalicylic acid in one tablet and the experimental value based on your titration. Finally, identify at least three sources of error for your data.