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Selecting Indicators for Acid–Base Titrations

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Introduction

Acids and bases vary in strengths and are normally classified as strong or weak. In any acid–base titration the neutralization, or equivalence point, occurs when the moles of acid in solution are equal to the moles of base. However, the pH of the solution at this point can vary widely and depends on the strengths of both the acid and the base. How is an indicator selected that fits a particular acid–base titration?

Concepts

- Weak acid
- Weak base
- Equivalence point
- Acid–base titration
- pH indicator
- Conjugate acid–base pairs

Background

In acid–base titrations, the plot of pH versus volume of titrant results in an S-shaped curve (see Figure 1).

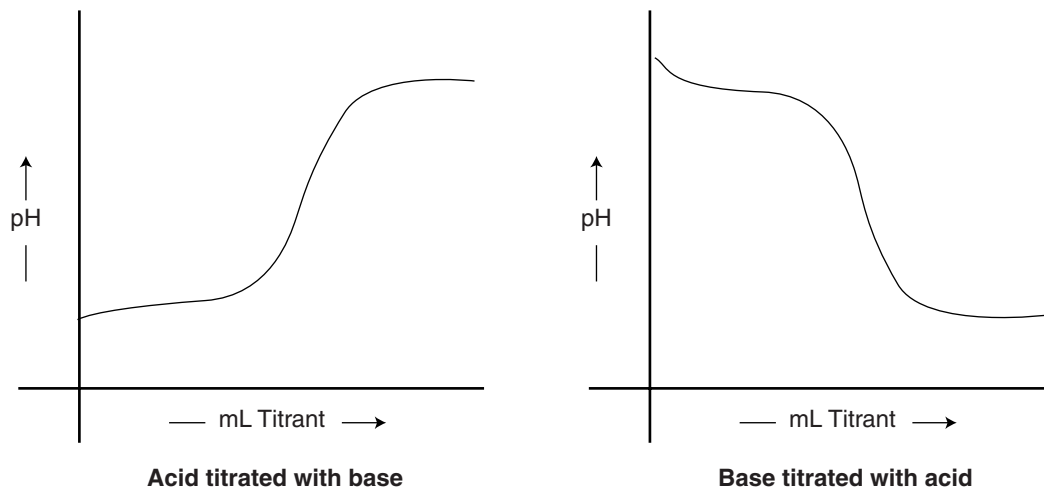


Figure 1.

The steepness of the curve and the pH value at the equivalence point depend on the strength of both the acid and the base. If both the acid and base are strong, the curve is very steep and the equivalence point pH value is 7.

If a *weak acid* is titrated by a strong base, the titration curve is less steep and the equivalence point pH value is >7. At the equivalence point,

$$\text{moles of acid (HA)} = \text{moles of base (OH}^- \text{) added} \quad \text{Equation 1}$$

or

$$M_{\text{HA}} \cdot V_{\text{HA}} = M_{\text{OH}^-} \cdot V_{\text{OH}^-} \quad \text{Equation 2}$$

The overall neutralization reaction is,



At this point, the initial moles of the weak acid (HA) have been completely converted to its *conjugate base* (A^-). This conjugate base is a weak base and equilibrates with water to form a basic solution.



K_b , for this reaction, is,

$$K_b = \frac{K_w}{K_a} \quad \text{or} \quad K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} \quad \text{Equation 3}$$

where K_w is 1×10^{-14} and K_a is the dissociation constant of the weak acid (HA).

The pH at the equivalence point is found by first calculating the pOH, or $-\log[\text{OH}^-]$, of this solution of the weak base A^- and water.

The initial concentration of A^- , before its reaction with water, is equal to the initial moles of weak acid, HA, present in the solution, divided by the volume of solution at the equivalence point.

When the weak base A^- reacts with water, at equilibrium,

$$[\text{HA}] = [\text{OH}^-] = x$$

$$\text{and } [\text{A}^-] = \frac{\text{initial moles of HA}}{\text{volume of solution at the equivalence point}} - x$$

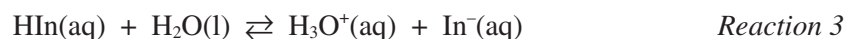
If $[\text{A}^-] \gg [\text{HA}]$, substituting these values into Equation 3 yields

$$[\text{OH}^-] = x = K_b \cdot [\text{A}^-] \quad , \quad \text{where } [\text{A}^-] = \frac{\text{initial moles HA}}{\text{volume of solution at equivalence point}}$$

Since $\text{pOH} = -\log[\text{OH}^-]$ and $\text{pH} + \text{pOH} = 14.00$,

$$\text{pH} = 14.00 - \text{pOH}$$

Once this pH value is determined, an appropriate indicator can be selected for the titration. Indicators are mostly complex organic molecules that are themselves weak acids. If the indicator is represented by HIn, then in solution,



$$\text{with } K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad \text{Equation 4}$$

The HIn form has one color in solution and the In[−] form has another. If Equation 3 is rearranged, then

$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{[\text{In}^-]}{[\text{HIn}]} \quad \text{Equation 5}$$

As base is added in the titration, H₃O⁺ ions are removed and the equilibrium shifts right, forming more In[−] ions. A color change starts to occur when [In[−]] is about one-tenth [HIn].

At this point,

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{1}{10}$$

In terms of pH

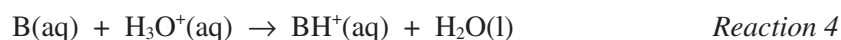
$$\text{p}K_a - \text{pH} = 1 \quad \text{or} \quad \text{pH} = \text{p}K_a - 1 \quad \text{Equation 6}$$

For a specific titration of an acid by a base, an indicator is selected that has a p*K*_a one unit above the pH value of the equivalence point. The color transition of the indicator is complete when,

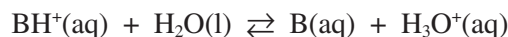
$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{10}{1}$$

Thus the transition range for most indicators is two pH units, or p*K*_a ± 1.

When a weak base is titrated with a strong acid, all the weak base (B) is converted to its conjugate acid (BH⁺) at the equivalence point.



The BH⁺ produced equilibrates with water to form an acidic solution.



$$K_a = \frac{K_w}{K_b} = \frac{[\text{H}_3\text{O}^+][\text{B}]}{[\text{BH}^+]} \quad \text{Equation 7}$$

At equilibrium of the weak acid BH⁺ and water,

$$[\text{B}] = x = [\text{H}_3\text{O}^+]$$

$$\text{and } [\text{BH}^+] = \frac{\text{initial moles of B}}{\text{volume of solution at equivalence point}}$$

if, at equilibrium, $[BH^+] \gg [B]$; then

$$[H_3O^+] = x = \sqrt{K_a \cdot [BH^+]}, \text{ where } [BH^+] = \frac{\text{initial moles of B}}{\text{volume of solution at equivalence point}} \quad \text{Equation 8}$$

As K_a increases, the pH at the equivalence point decreases. Relating this to the K_b values, the weaker the base, the lower the pH at the equivalence point.

In basic solution, the indicators initially exists in the In^- form. Now the color transition occurs when the HIn concentration is one-tenth the In^- concentration, or,

$$\frac{[In^-]}{[HIn]} = \frac{10}{1}$$

$$pH = pK_a + 1 \quad \text{Equation 9}$$

Experimental Overview

The appropriate indicators are selected for two titrations—a weak acid solution titrated with a strong base solution and a weak base solution titrated with a strong acid solution. The indicators are added to the solutions and the solutions are titrated. Titration curves of pH versus volume of titrant are generated and used to verify the appropriateness of the selected indicators.

Pre-Lab Questions and Calculations

1. In Part 1 of this laboratory, 25.0 mL of a 0.100 M solution of the weak acid acetic acid, CH_3COOH , is titrated with a 0.100 M solution of the strong base sodium hydroxide, $NaOH$. K_a of acetic acid is 1.8×10^{-5} .
 - a. Calculate the pH of the equivalence point. Enter this value in the Part 1 Data Table.
 - b. Five indicators, along with their pK_a values and their color change ranges, are listed in the table below.

	pK_a	Color Transition Range (pH)												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Methyl Orange	3.40	Red												Yellow
Methyl Red	4.95	Red												Yellow
Phenolphthalein	9.4													Red
Bromthymol Blue	7.1													Blue
Thymolphthalein	10.0													Blue

Based on the pH calculated in 1a., select the appropriate indicator for the weak acid–strong base titration. Enter the selection in the Part 1 Data Table.

2. In Part 2, 25.0 mL of a 0.10 M solution of the weak base ammonia, NH_3 , is titrated with a 0.10-M solution of the strong acid hydrochloric acid, HCl . K_b of ammonia is 1.8×10^{-5} .
 - a. Calculate the pH of the equivalence point. Enter this value in the Part 1 Data Table.
 - b. Select the appropriate indicator for the weak base–strong acid titration. Enter the selection in the Part 2 Data Table.
3. 25 mL of a 0.10 M solution of the weak acid hydrofluoric acid, HF , is titrated with a 0.10 M solution of the weak base ammonia, NH_3 . Will the pH at the equivalence point be less than 7, equal to 7, or greater than 7? Explain. K_a for HF is 7.2×10^{-4} and K_b for NH_3 is 1.8×10^{-5} .

Materials

Sodium hydroxide solution, NaOH , 0.10 M, 100 mL	pH sensor or pH meter
Hydrochloric acid solution, HCl , 0.10 M, 100 mL	Buret, 50-mL or 25-mL
Acetic acid solution, CH_3COOH , 0.10 M, 75 mL	Ring stand and buret clamp
Ammonia solution, NH_3 , 0.10 M, 75 mL	Wash bottle
Bromthymol blue indicator solution, 0.04%, 1 mL	Beakers, 250-mL, 2
Thymolphthalein indicator solution, 0.04%, 1 mL	Beakers, 150-mL, 2
Phenolphthalein indicator solution, 0.5%, 1 mL	Volumetric pipet, 25-mL
Methyl red indicator solution, 0.02%, 1 mL	Magnetic stirrer and spin bar
Methyl orange indicator solution, 0.1%, 1 mL	Distilled or deionized water

Safety Precautions

All the acids and bases used in this lab are irritating to eyes, skin, and other body tissues. The phenolphthalein solution is a flammable liquid, a fire risk, and is moderately toxic. Methyl orange indicator solution is toxic by ingestion. The thymolphthalein solution is a flammable liquid and a fire risk. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the lab. Clean up all spills immediately.

Procedure

Tips

1. Label all solutions.
2. Practice pipetting technique.
3. Always rinse glassware with distilled or deionized water.

Part 1. Titration of a Weak Acid with a Strong Base

1. Place about 75 mL of 0.10 M acetic acid solution in a clean 250-mL beaker.

- Using a clean 25-mL volumetric pipet, quantitatively transfer 25.0 mL of 0.10 M acetic acid solution to a clean 150-mL beaker (see Figure 2).

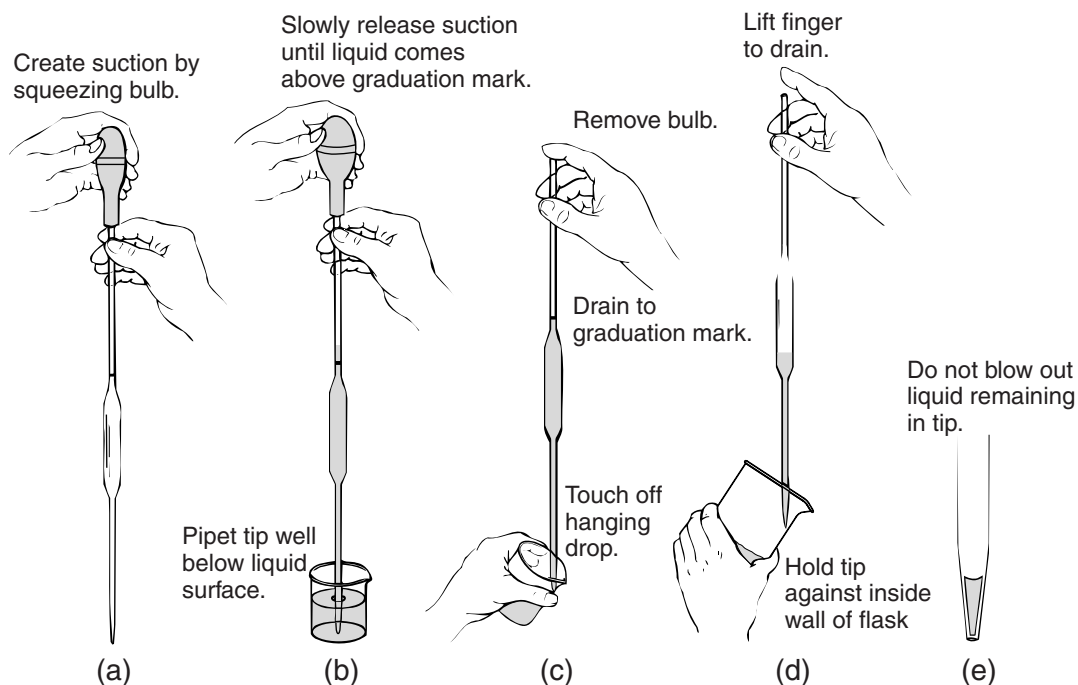


Figure 2. Using a volumetric pipet.

- Obtain about 100 mL of the 0.10 M NaOH solution in a clean, 250-mL beaker.
- Clean a 50-mL buret thoroughly with tap water, then rinse it with several small portions of the standard NaOH solution, being sure to run some solution through the tip.
- Attach the buret clamp to the ring stand. Place the buret in the buret clamp.
- Fill the buret above the 0-mL mark, then lower the meniscus back to the 0-mL mark.
- Set up a pH meter and electrode on the ring stand. Calibrate the pH meter using a buffer solution of pH 7.00. Rinse the electrode well with distilled water.
- Set the beaker containing the acetic acid solution on a magnetic stirrer so that the buret tip is just below the lip of the beaker. Clamp the pH electrode so it is submerged in the acid solution (Figure 3). Be sure the stir bar does not hit the electrode. Set the stir bar gently spinning.
- When the pH reading has stabilized, record the initial pH of the solution in Part 1 Data Table.
- Add 3 drops of the indicator selected for this titration in the *Pre-Lab Calculations* section. Record the solution color in the Part 1 Data Table.
- Add about 1 mL of sodium hydroxide solution to the beaker.

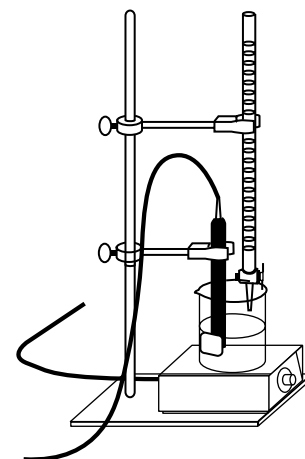


Figure 3. Setup.

- Record the exact buret reading in Part 1 Data Table.
- Record the pH and the color of the solution next to the buret reading in the Part 1 Data Table.
 - Add another 1-mL increment of sodium hydroxide solution. Record the buret reading, the pH, and the solution color in Part 1 Data Table.
 - Continue adding sodium hydroxide in 1-mL portions. Record the buret reading, the pH, and the solution color after each addition.
 - When the pH begins to increase by more than 0.3 pH units after an addition, decrease the portions of sodium hydroxide added to about 0.2 mL.
 - Continue adding sodium hydroxide in about 0.2 mL increments. Record the buret reading, the pH, and the solution color after each addition.
 - When the pH change is again about 0.3 pH units, resume adding the sodium hydroxide in 1-mL increments. Continue to record both the buret reading, the pH, and the solution color after each addition.
 - Stop the titration when the pH of the solution is greater than 12. Record the final volume of solution in the buret, final pH, and solution color.
 - Repeat the titration. If the indicator selected did not change color at the equivalence point in the first titration, review the *Pre-Lab Calculations* and select another indicator.

Part 2. Titration of a Weak Base with a Strong Acid

- Place about 75 mL of 0.10 M ammonia (NH_3) solution in a clean 250-mL beaker.
- Using a clean 25-mL volumetric pipet, quantitatively transfer 25.0 mL of 0.10 M NH_3 solution to a clean 150-mL beaker.
- Obtain about 100 mL of 0.10 M hydrochloric acid (HCl) solution in a clean, 250-mL beaker.
- Rinse the 50-mL buret with three small portions of deionized water, then rinse it with several small portions of 0.10 M HCl solution. Place the buret back in the buret clamp.
- Fill the buret with 0.10 M HCl solution above the 0-mL mark, then lower the meniscus back to zero.
- Set the beaker containing the 0.10 M NH_3 solution on a magnetic stirrer. Clamp the pH electrode so it is submerged in the basic solution. Be sure the stir bar does not hit the electrode. Set the stir bar gently spinning.
- When the pH reading has stabilized, record the initial pH of the solution in Part 2 Data Table.
- Add three drops of the indicator selected for this titration in the *Pre-Lab Calculations* section. Record the solution color in the Part 2 Data Table.
- Add about 1 mL of 0.1 M HCl solution to the beaker. Record the exact buret reading in Part 2 Data Table.
- Record the pH of the solution and the solution color next to the buret reading in the Part 2 Data Table.

11. Add another 1-mL increment of hydrochloric acid solution. Record the buret reading, the pH, and the solution color in Part 2 Data Table.
12. Continue adding hydrochloric acid in 1-mL portions. Record both the buret reading, the pH, and the solution color after each addition.
13. When the pH begins to decrease by more than 0.3 pH units after an addition, decrease the portions of 0.10 M HCl added to about 0.2 mL.
14. Continue adding 0.10 M HCl in about 0.2 mL increments. Record the buret reading, the pH, and the solution color after each addition.
15. When the pH change is again about 0.3 pH units, resume adding the 0.10 M HCl in 1-mL increments. Continue to record the buret reading, the pH, and the solution color after each addition.
16. Stop the titration when the pH of the solution is less than 2. Record the final volume of solution in the buret, the final pH, and the final solution color.
17. Repeat the titration. If the indicator selected did not change color at the equivalence point in the first titration, review the *Pre-Lab Calculations* and select another indicator.

Disposal

Dispose of all solutions as directed by your instructor.

Post-Lab Graphs and Calculations

Graph the pH versus the mL of titrant for each of the titrations. Make sure the graph is large enough to reflect the care taken with measuring the pH and volume. Draw the best fitting smooth curve for the data. Label the equivalence point. Indicate the indicator color for each data point. Were the indicators selected appropriate for the two titrations? If not, why?