

## **APPENDICES**

### **TOPIC 5: Acids and Bases**



### Appendix 1: Selected Neutralization Indicators

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Indicator	Colour Change (lower pH listed first)	Approximate pH Range of colour change
Picric acid	colourless to yellow	0.1 to 0.8
Paramethyl red	red to yellow	1.0 to 3.0
2,6-Dinitrophenol	colourless to yellow	2.0 to 4.0
Bromophenol blue	yellow to blue	3.0 to 4.6
Congo red	blue to red	3.0 to 5.0
Methyl orange	red to yellow	3.1 to 4.4
Ethyl orange	red to yellow	3.4 to 4.5
Alizarin red S	yellow to purple	3.7 to 5.0
Methyl red	red to yellow	4.2 to 6.2
Methyl purple	purple to green	4.8 to 5.4
Propyl red	red to yellow	4.6 to 6.6
Paranitrophenol	colourless to yellow	5.9 to 7.0
Bromocresol purple	yellow to purple	5.2 to 6.8
Bromothymol blue	yellow to blue	6.0 to 7.6
Brilliant yellow	yellow to orange	6.6 to 8.0
Neutral red	red to amber	6.7 to 8.0
Phenol red	yellow to red	6.7 to 8.4
Metanitrophenol	colourless to yellow	6.7 to 8.6
Phenolphthalein	colourless to pink	8.3 to 10.0
Thymolphthalein	colourless to blue	9.4 to 10.6
Alizarin blue-5	amber and green to blue green	11.0 to 12.0
2,4,6-Trinitrotoluene	colourless to orange	12.0 to 14.0

Source: *Quantitative Chemical Analysis*: Robert B. Fischer, Published by W.B. Saunders Company, Philadelphia and London, 1965, p 265. (used with permission)

## Appendix 2: Lab - Indicators and pH

The acidity (concentration of  $H^+$ ) or alkalinity (concentration of  $OH^-$ ) of an aqueous solution is an important factor in describing the solution's properties. The measurement of the  $H^+$  or  $OH^-$  in a solution can be accomplished in several ways.

Use of a pH meter The pH meter is an electronic device which compares voltage in a solution to that of a standard. The acidity or alkalinity is read directly from a digital or analog meter. The device is accurate and fast, but relatively expensive.

Use of indicator paper Indicator paper is ordinary filter paper which has been soaked in a solution of dye(s) called indicator(s). This indicator changes colour when the concentration of  $H^+$  reaches a certain level. While test paper is relatively inexpensive, it is difficult to follow any continuous change in the pH of the solution since the paper must be dipped in and out repeatedly.

Use of an indicator solution An indicator solution changes colour at a specific pH. Mixtures of indicators can be used to provide a continuously changing picture corresponding to changes in pH. In this lab, three individual indicators (bromthymol blue, phenolphthalein, and methyl orange) and a standard mixture of indicators (universal) will be used. The standard universal indicator is a mixture of organic dyes which change colour and allow for a fairly accurate approximation of the whole number pH value of a test solution.

### Materials and Apparatus

0.1 mol/L NaOH	0.1 mol/L HCl
distilled water	universal indicator
bromthymol blue indicator	phenolphthalein indicator
methyl orange indicator	well plate
eye droppers	

### Procedure

1. Place the well plate on white paper with the lettered columns on the left. Place 9 drops of distilled water into wells #2 through #11 of rows A, B, C, and D.
2. Add 10 drops of 0.1 mol/L HCl to wells A1, B1, C1, and D1.
3. Add 10 drops of 0.1 mol/L NaOH to wells A12, B12, C12, and D12.
4. Transfer 1 drop of hydrochloric acid from well A1 to well A2. Mix by drawing the contents of well A2 into the eye dropper and then returning the liquid to well A2.

5. Transfer one drop from well A2 to well A3, again by mixing by drawing the contents of well A3 into an eye dropper and returning the contents to well A3. Continue the serial dilution in this manner through and including well #6.
6. Repeat steps 4 and 5 for rows B, C, and D.
7. Transfer 1 drop of sodium hydroxide solution from well A12 to well A11. Mix by drawing up the contents of well 11 into an eye dropper and then returning the liquid to well 11.
8. Now transfer one drop from well A11 to well A10, again mixing by drawing the contents of well A10 into an eye dropper and returning the contents to well A10. Continue the serial dilution in this Manner, backwards through and including well #8.
9. Repeat steps 7 and 8 for rows B, C, and D.

You now have 4 rows of diluted solutions containing varying amounts of acid and base, each  $1/10^{\text{th}}$  of the acid of the well to its left and  $1/10^{\text{th}}$  the base of the well to its right. Well numbers indicate the approximate pH of the solutions in each well, e.g., well #4 has a pH of 4 and well #9 has a pH of 9.

10. Add 1 drop of universal indicator to each well in row A.
11. Add 1 drop of methyl orange to each well in row B.
12. Add 1 drop of phenolphthalein to each well in row C.
13. Add 1 drop of bromthymol blue to each well in row D.

### **Analysis**

1. What is the significance of the colour changes in each row?
2. Which would be a good indicator for general use?
3. Which would be a good indicator for a HCl/NaOH titration?
4. Which would be a poor indicator for a HCl/NaOH titration? Why?

## Appendix 3 : Measuring pH – Student Procedure

### Introduction:

The pH of an aqueous solution can be measured several ways including:

- with commercially prepared pH paper
- with a pH meter, or pH probe connected to a calculator or microcomputer interface
- with an acid-base indicator solution

An acid-base indicator is a substance whose color in solution depends upon the hydronium ion concentration.

Acid-base indicators change color from their acid form to their base form over a specific range of pH.

**Objective:** To determine the colors of three different indicators and a 'universal' indicator (a mixture of indicators) over a range of pH.

### Procedure:

1. Place a 96-well microplate on a piece of white paper with the numbered columns on the top and the lettered rows on the left. (The white paper will make the color changes more visible.)
  2. In rows A, C, E, and G, add 9 drops of distilled water to each of the wells #2 through #11.
  3. Place 10 drops of a 0.1 mol L<sup>-1</sup> aqueous hydrochloric acid (HCl(aq)) solution in well #1 of rows A, C, E, and G.
  4. Place 10 drops of a 0.1 mol L<sup>-1</sup> aqueous sodium hydroxide (NaOH) solution in well #12 of rows A, C, E, and G.
  5. Transfer one drop of 0.1 mol L<sup>-1</sup> HCl(aq) solution from well A1 to well A2. Mix thoroughly by stirring with a new toothpick or clean glass stirrer. (If a glass stirrer is used, rinse it carefully with distilled water and wipe it on a dry paper towel before reusing it.) Continue by transferring one drop from well #A2 to well #A3, and mixing thoroughly. Continue from well to well until you reach well #6. This will be the last acidic dilution.
  6. Continue this procedure (serial dilution) for each of the rows C, E, and G.
  7. Repeat the dilution procedure using the 0.1 mol L<sup>-1</sup> NaOH(aq) solution in the same rows as the acid dilution, working backwards from well #12 to well #8, making #8 the last basic dilution.
- You now have four rows each of diluted acidic and basic solutions. Show that the pH of the acidic solutions are approximately 1, 2, 3, 4, 5, and 6 respectively in wells 1 through 6, and of the pH of the basic solutions are approximately 9, 10, 11, 12, and 13 respectively in wells 8 through 12.
8. Add 1 drop of universal indicator solution to each well in row A.
  9. Add 1 drop of methyl orange indicator solution to each well in row C.
  10. Add 1 drop of bromothymol blue indicator solution to each well in row E.
  11. Add 1 drop of phenolphthalein indicator solution to each well in row G.
  12. Record your observations for each row.
  13. Construct a table that correlates the pH range with a color change.
  14. Describe how you could use the results from this experiment to estimate the pH of an aqueous solution.

## Measuring pH – Teacher Support

### Preparation of Indicator Solutions:

These solutions can be prepared in advance and are stable for at least 6 months.

Bromothymol blue:

Dissolve 0.04 g of the sodium salt of bromothymol blue (3',3''-dibromo-thymolsulfonephthalein, sodium salt) in 100 L of distilled water.

Methyl orange:

Dissolve 0.01 g of methyl orange (sodium 4-[4-(dimethylamino)phenylazo]-benzenesulfonate) in 100 mL of distilled water.

Phenolphthalein:

Dissolve 0.05 g of phenolphthalein (3,3-bis(*p*-hydroxyphenyl)phthalide) in 50 mL of 95% ethanol, and dilute the resulting solution to 100 mL with distilled water.

### Yamada's universal indicator:

Dissolve 0.0025 g of thymol blue, 0.06 g of methyl red, 0.030 g of bromothymol blue, and 0.05 g of phenolphthalein in 50 mL of 95% ethanol. Add 0.01 mol L<sup>-1</sup> aqueous sodium hydroxide solution until the mixture is green, and dilute the resulting solution to 100 mL with distilled water.

### Appendix 4: Relative Strengths of Acids

Acid	Reaction	Ka
Perchloric acid	$\text{HClO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$	very large
Hydriodic acid	$\text{HI} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{I}^-$	very large
Hydrobromic acid	$\text{HBr} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Br}^-$	very large
Hydrochloric acid	$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$	very large
Nitric acid	$\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$	very large
Sulfuric acid	$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^-$	very large
Oxalic acid	$\text{HOOC-COOH} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HOOC-COO}^-$	$5.4 \times 10^{-2}$
Sulfurous acid	$\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_3^-$	$1.7 \times 10^{-2}$
Hydrogen sulfate ion	$\text{HSO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$	$1.3 \times 10^{-2}$
Phosphoric acid	$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$	$7.1 \times 10^{-3}$
Ferric ion	$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	$6.0 \times 10^{-3}$
Hydrogen telluride	$\text{H}_2\text{Te} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HTe}^-$	$2.3 \times 10^{-3}$
Hydrofluoric acid	$\text{HF} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{F}^-$	$6.7 \times 10^{-4}$
Nitrous acid	$\text{HNO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_2^-$	$5.1 \times 10^{-4}$
Hydrogen selenide	$\text{H}_2\text{Se} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSe}^-$	$1.7 \times 10^{-4}$
Chromic ion	$\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	$1.5 \times 10^{-4}$
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{COO}^-$	$6.6 \times 10^{-5}$
Hydrogen oxalate ion	$\text{HOOC-COO}^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OOC-COO}^{2-}$	$5.4 \times 10^{-5}$
Acetic acid	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	$1.8 \times 10^{-5}$
Aluminum ion	$\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	$1.4 \times 10^{-5}$
Carbonic acid	$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^-$	$4.4 \times 10^{-7}$
Hydrogen sulfide	$\text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HS}^-$	$1.0 \times 10^{-7}$
Dihydrogen phosphate ion	$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$	$6.3 \times 10^{-8}$
Hydrogen sulfite ion	$\text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SO}_3^{2-}$	$6.2 \times 10^{-8}$
Ammonium ion	$\text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NH}_3$	$5.7 \times 10^{-10}$
Hydrogen carbonate ion	$\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-}$	$4.7 \times 10^{-11}$
Hydrogen telluride ion	$\text{HTe}^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Te}^{2-}$	$1.0 \times 10^{-11}$

Hydrogen peroxide	$\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HO}_2^-$	$2.4 \times 10^{-12}$
Monohydrogen phosphate ion	$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{PO}_4^{3-}$	$4.4 \times 10^{-13}$
Hydrogen sulfide ion	$\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{S}^{2-}$	$1.2 \times 10^{-15}$
Water	$\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$	$1.8 \times 10^{-16}$
Hydroxide ion	$\text{OH}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{O}^{2-}$	$< 10^{-36}$
Ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_2^-$	very small

## Appendix 5: QUANTITATIVE ANALYSIS: ACID-BASE TITRATION

- Purpose:**
- To standardize a base solution using a stock acid solution by the method of titration.
  - Given an unknown mass of a solid, prepare a 100 mL aqueous solution of that acid.
  - Titrate the unknown acid solution with a base of known concentration and determine the number of grams of solid acid to 0.001 g.

### Procedure

#### Part A

- Each student will be assigned two burets, one on the left for acid, and the other on the right for base. Before using the burets, they should be carefully washed with soap and water, then rinsed with tap water to remove all soap. The burets should then be rinsed with 15 mL portions of distilled water, ensuring there are no air bubbles in the tips of the burets. Finally, the burets should be rinsed with several small (10–15 mL) aliquots of each solution.
- Fill a buret with the acid and the other with base. Read each buret, to determine the initial acid and base volumes, to the nearest 0.01 mL.
- About 10 – 15 mL of acid should be introduced into a clean 250 mL erlenmeyer flask, followed by about 10 mL of distilled water to rinse down the sides. Read the volume of the acid buret and record as the final acid reading. Add about 3 drops of phenolphthalein indicator to the flask. A new clean flask should be used for each trial.
- While continuously swirling the flask, the base should be added SLOWLY until a pale lasting pink colour persists, indicating the endpoint. NOTE: As the end point is approached, the colour disappears more slowly until finally the pale pink colour persists. The volume should then be carefully read from the base buret and recorded as the final base volume.
- This entire process should be repeated as many times ( minimum 4 ) as needed to obtain consistency of data to 3 sig figs for the base concentration.
- Select your three best trials and put them into a data table. Show calculations for each trial. Calculate the average of the three trials. Record this average.

## Part B

1. Obtain a vial containing a sample of sulfamic acid with the formula  $\text{H}_2\text{NSO}_3\text{H}$  and having a molar mass of 97.09 g/mol.
2. Transfer the acid to a 100 mL volumetric flask. Fill the flask about  $\frac{1}{2}$  with water and swirl until the solid dissolves completely, then fill with water exactly to the 100 mL mark on the flask. Great care should be taken with the acid sample as only one sample will be handed out per student. The 100 mL sample is enough for 5 - 8 titrations which should be enough to complete the determination.
3. Once the acid solution has been prepared, the same procedure will be used as for part A of this experiment. Only this time, the sulfamic acid will be used instead of the hydrochloric acid and a new base stock standard solution will be used. The concentration of the base can be read off the stock solution.
4. Report three of the best trials and record as in Part A. The mass must be calculated to 0.001 g.

### **Calculations and Follow-up Questions:**

1. Record values of acid and base volumes from Part A in a data table.

**Titration Data Table** - \_\_\_\_\_

Trial	Buret Reading	Acid	Base
Trial 1	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 2	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 3	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 4	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 5	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 6	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 7	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 8	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		

2. Calculate the concentration of the base used. Show all work.

3. Record values of acid and base values from Part B in a data table.

**Titration Data Table –**

Trial	Buret Reading	Acid	Base
Trial 1	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 2	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 3	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 4	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 5	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 6	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 7	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		
Trial 8	Final Buret Reading		
	Initial Buret Reading		
	Total Volume		

4. Calculate the concentration of the sulfamic acid in your sample. Show all your work.
  
  
  
  
  
  
  
  
  
  
5. Calculate the mass of your sample of sulfamic acid. Present the average of your best three trials. Show all your work.
  
  
  
  
  
  
  
  
  
  
3. When an end point is reached in an acid-base titration what does this indicate about the concentration of the  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$ .
  
  
  
  
  
  
  
  
  
  
4. What would you expect the pH of the solution to be, just at the point at which the phenolphthalein turns pink?
  
  
  
  
  
  
  
  
  
  
5. Why is an indicator solution so important to use for titrations?
  
  
  
  
  
  
  
  
  
  
6. What does this statement mean: "The relative volumes required in a titration vary inversely with the concentrations of the solutions."?

## Appendix 6 : Analysis of Household Vinegar

**Objective:** To determine the percent acetic acid by mass of household vinegar.

**Introduction:** Vinegar contains acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) as the active ingredient. Most vinegar samples are described as 5%.

**Procedure:**

1. Pipet 5.0 mL of your vinegar sample into a 250-mL Erlenmeyer flask. Add 25 mL of distilled water to the flask. Add 2 or 3 drops of phenolphthalein indicator solution.
2. Rinse and fill your buret with your standardized solution of sodium hydroxide. Record the level of the solution in the buret.
3. Slowly add the base solution from the burette to the flask containing the vinegar, swirling the flask as you titrate. When the pink color starts to disappear more slowly, begin adding the base solution dropwise.
4. Stop the titration when the first trace of faint pink remains for 20 - 30 seconds after swirling. Wait about 30 seconds, then record the level in the burette estimating to within half the smallest gradation (i.e., 0.01, 0.02, 0.05, etc.).
5. Repeat the titration until you can reproduce the volume added to  $\pm 0.1$  mL.
6. Make the calculations necessary to complete the following table. Assume the density of vinegar is  $1.00 \text{ g mL}^{-1}$ .

**Data:**

		Trial #1	Trial #2	Trial #3
Buret reading:	Final:	_____	_____	_____
	Initial:	_____	_____	_____
	Volume used:	_____	_____	_____

Concentration of standardized NaOH: \_\_\_\_\_

**Calculations:**

Chemical amount (moles)  
of  $\text{HC}_2\text{H}_3\text{O}_2$  in sample: \_\_\_\_\_

Mass of  $\text{HC}_2\text{H}_3\text{O}_2$  in sample: \_\_\_\_\_

Per cent  $\text{HC}_2\text{H}_3\text{O}_2$  by mass: \_\_\_\_\_

## Appendix 6 : Analysis of Household Vinegar (editable version)

**Objective:** To determine the percent acetic acid by mass of household vinegar.

**Introduction:** Vinegar contains acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) as the active ingredient. Most vinegar samples are described as 5%.

### Procedure:

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2. Rinse and fill your buret with your standardized solution of sodium hydroxide. Record the level of the solution in the buret.
3. Slowly add the base solution from the burette to the flask containing the vinegar, swirling the flask as you titrate. When the pink color starts to disappear more slowly, begin adding the base solution dropwise.
4. Stop the titration when the first trace of faint pink remains for 20 - 30 seconds after swirling. Wait about 30 seconds, then record the level in the burette estimating to within half the smallest gradation (i.e., 0.01, 0.02, 0.05, etc.).
5. Repeat the titration until you can reproduce the volume added to  $\pm 0.1$  mL.
6. Make the calculations necessary to complete the following table. Assume the density of vinegar is  $1.00 \text{ g mL}^{-1}$ .

### Data:

Trial #1 Trial #2 Trial #3

Buret reading: Final:

Initial:

Volume used:

Concentration of standardized NaOH: \_\_\_\_\_

### Calculations:

Chemical amount (moles)  
of  $\text{HC}_2\text{H}_3\text{O}_2$  in sample:

Mass of  $\text{HC}_2\text{H}_3\text{O}_2$  in sample:

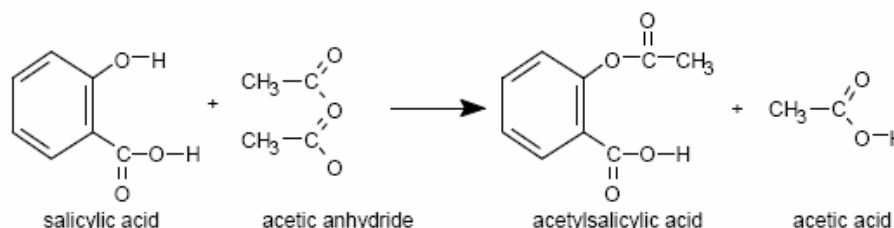
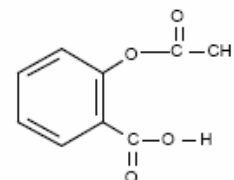
Per cent  $\text{HC}_2\text{H}_3\text{O}_2$  by mass:

## Appendix 7: Analysis of Aspirin

### Introduction:

Aspirin™ (the trade name for the Bayer product) is the common name given to acetylsalicylic acid, sometimes abbreviated ASA. The structural formula is given to the right.

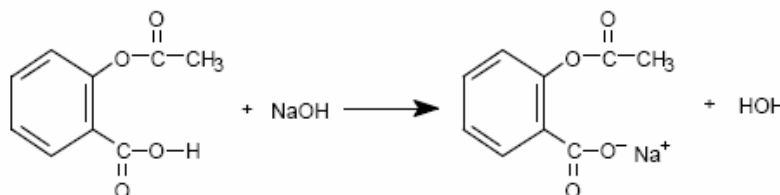
Pure ASA can be synthesized by treating salicylic acid with acetic anhydride in the presence of a trace of either sulfuric or phosphoric acids.



The product is removed from the reaction mixture by crystallization. The crude ASA must be purified by washing to remove excess by-products and then re-crystallized in the pure state.

Aspirin™ tablets are made by blending the pure ASA with filler (inert material), which gives body to the tablet so that it can be pressed and shaped.

The purpose of this analysis is to determine the degree of purity of various commercial products. The analysis is based on titration of the ASA tablet with a standard sodium hydroxide solution. During this reaction,  $H^+$  ion is transferred from the acid to the reacting base,  $OH^-$ . The following equation illustrates the reaction:



Titration is continued until an endpoint is reached, as indicated by the phenolphthalein indicator. The percent of ASA present can then be calculated.

### Procedure:

- Determine the mass of a single ASA tablet to the nearest 0.01 g by direct weighing.
- Place the tablet in a 250 mL conical flask and add approximately 15 mL of water and 15 mL of ethanol (ethyl alcohol). Use a glass rod to crush the tablet. Agitate to dissolve the tablet. Complete solution may not be accomplished prior to titration with base solution.
- Add approximately 3 drops of phenolphthalein indicator solution. No color change should be seen.
- Carefully fill a 50 mL buret with standard  $0.1 \text{ mol L}^{-1}$  sodium hydroxide solution. Record the exact concentration of the standard sodium hydroxide solution.
- Record the level of sodium hydroxide solution in the buret. Place the flask containing the ASA sample under the buret.
- Add small volumes of sodium hydroxide solution, while swirling the flask. Continue adding sodium hydroxide solution until the first indication of a phenolphthalein endpoint has been reached, as indicated by a light pink color throughout the solution in the flask. This color should remain without fading upon swirling.
- Record the level of the solution in the buret.

### Calculations:

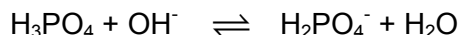
Calculate the percent of ASA in your tablet. The formula mass of ASA is  $180 \text{ g mol}^{-1}$ , and each molecule transfers 1 hydrogen ion to a base.

## APPENDIX 8: POTENTIOMETRIC ANALYSIS OF ACID IN SOFT DRINKS: COLA VS. UNCOLA

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(Suggested time allotment: 2 lab periods)

Phosphoric acid is a common ingredient in cola drinks; it provides a taste that is both sweet and sour, but does not compete with other flavors. There is some variability in both the amount and composition of the acid in cola drinks. The composition is affected by the equilibrium



In this experiment, we will determine the  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  in a sample of cola drink using a potentiometric titration. We choose a potentiometric detection method over an acid-base indicator for two reasons: (1) the color of the cola obscures indicator changes, and (2) the use of a pH meter permits a more accurate location of the equivalence points in a titration than an indicator.

We will also determine the citric acid concentration in an “uncola” drink. Citric acid, which is also tribasic, is another common ingredient in many soft drinks. The acid dissociation constants for phosphoric and citric acids are as follows:

	Phosphoric acid	Citric acid
$K_1$	$7.11 \times 10^{-3}$	$7.44 \times 10^{-4}$
$K_2$	$6.32 \times 10^{-8}$	$1.73 \times 10^{-5}$
$K_3$	$7.10 \times 10^{-13}$	$4.02 \times 10^{-7}$

From these data, it is clear that the constants for phosphoric acid are more than a factor 1,000 apart and three distinct endpoints can therefore be observed in a titration. In contrast, the citric acid constants are closer together and the titration has no definite breaks between the endpoints. Moreover, several of the citric and phosphoric acid endpoints are mutually close. It is therefore advisable to carry out this experiment with soft drinks that do not contain both phosphoric and citric acid. A possible choice is Coca Cola for the phosphoric acid determination, and Squirt for the citric acid determination. If you choose other brands, you should make sure from the ingredient panel that only one or the other of the acids is present. The drinks also should not contain lactic acid or aspartame (“Nutrasweet”) so do not choose diet drinks!)

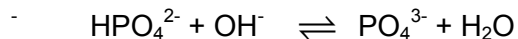
The potentiometric response of the glass electrode is described by the equation:

$$E_{\text{glass}} = k - 0.059 \text{ pH}$$

where  $k$  is a constant. Clearly, there is a simple linear relationship between the measured potential and the pH of the solution. For convenience, the pH meter is calibrated in pH units, so that the appropriate values can be read off directly.

You will calibrate the meter with pH 4 and 7 (or 10) buffers, following the instructions that are provided with the pH meter. Once the meter is calibrated, the pH of the  $\text{H}_3\text{PO}_4$  solution is easily followed as a function of added NaOH.

At pH 10.5 - 11, the glass electrode begins to respond to other ions (mainly  $\text{Na}^+$  in this case) since so few  $\text{H}_3\text{O}^+$  ions remain. This effect, which makes it appear that the pH is lower than it really is, is called the *alkaline error*. Its occurrence makes it advisable not to carry the titration beyond pH 10.5, meaning that you will not observe the third equivalence point of phosphoric acid:



### **Prelaboratory Assignment:**

The phosphoric acid in a 100.00-mL sample of cola drink was titrated with 0.1025 N NaOH. If the first equivalence point occurred after 13.11 mL of base was added, and the second equivalence point occurred after 28.55 mL of base, calculate the concentrations of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  in the cola sample. (Hint: where would the second equivalent point have occurred if only  $\text{H}_3\text{PO}_4$  were present?)

### **Apparatus**

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- stirrer and (large) stir bar
- pH meter and glass electrode
- two 250 mL beakers
- 50-mL buret
- 25-mL pipet
- 1000-mL bottle
- 25-mL graduated cylinder
- 1000-mL boiling flask
- stirring rod
- 400-mL beaker
- watch glass

### **Chemicals**

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- sodium hydroxide
- KHP
- cola unknown (e.g., Coca Cola)
- uncola unknown (e.g., Squirt)
- pH 4 and 7 buffers
- phenolphthalein indicator

## Procedure

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1. Standardize the pH meter with the buffers. See page 40 for procedure.
2. Prepare a standard 0.10 N NaOH solution as described in Experiment 1 (using a KHP primary standard). For the titration, use your pH electrode in conjunction with the phenolphthalein indicator and compare the electrode response to the indicator color change. Add small increments of titrant, reading both the stabilized pH value and the total volume added after each addition. Initially, the additions should be large enough to cause pH changes of about 0.2 units. When the pH starts to change rapidly, reduce the size of the NaOH aliquots. As you near the equivalence point, the pH will change considerably upon the slightest addition of base. To develop the entire titration curve (pH vs. volume of titrant), you need to proceed somewhat beyond the equivalence point. The electrode response is going to be the principal indicator of the endpoint in this experiment, but you should observe that the indicator changes color at the point where the greatest pH change occurs (note this volume). Any difference is called the indicator error. It should be small. Stop the titration at pH 10.5.
3. Add 100.00 mL of cola to a 250-mL beaker and cover it with a clean watch glass. Bring the solution just to boiling and keep it warm for five minutes. This expels the  $\text{CO}_2$  which otherwise would interfere with the titration of  $\text{H}_3\text{PO}_4$ . Cool the solution by placing ~200 mL of cold water in a 400-mL beaker and carefully resting the beaker with the cola in the cold water.
4. Rinse the electrodes. Refill the buret with the NaOH.
5. Place the glass electrode in the beaker. Add the stir bar and enough water to cover the electrode. Start the stirrer.
6. Proceed with the titration of the cola solution as you did for the NaOH standardization (except that there is no indicator here). Expect two equivalence points, one near pH 4 and the other near pH 8. Continue to pH 10.5.
7. Repeat steps 3-6 with the uncola. Now only one equivalence point should be found, near pH 6.

## Calculations

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1. Plot pH (ordinate, *i.e.*, y-axis) vs. volume of NaOH (abscissa, *i.e.*, x-axis) for the standardization and the two unknowns.
2. Construct first-derivative plots for these titrations. This is accomplished by plotting  $(\text{pH}_2 - \text{pH}_1)/(V_2 - V_1)$  vs.  $(V_1 + V_2)/2$ , where  $V_1$  and  $V_2$  are two successive titration volumes (totals) and  $\text{pH}_1$  and  $\text{pH}_2$  are the corresponding pH values. These plots have peaks where the original graphs have inflection points (*i.e.* the end points of the titrations). Use them to estimate the equivalence points.
3. Calculate the molarity of the titrant.

4. Use the equivalence point volumes obtained for the cola titration, along with the NaOH molarity, to calculate the moles of  $\text{H}_3\text{PO}_4$  present. Remember that at the first equivalence point one proton has been titrated, while at the second equivalence point, two protons have reacted. If your results show that  $V_{\text{eq}2} > 2 V_{\text{eq}1}$ , then not only  $\text{H}_3\text{PO}_4$  but also  $\text{H}_2\text{PO}_4^-$  was in present in the drink (see Prelab Assignment). Calculate the concentrations of both.
5. Calculate the concentration of citric acid in the uncola.

### Follow-up Questions

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1. In the phosphoric acid titration, could  $V_{\text{eq}2} < 2V_{\text{eq}1}$ ? Explain.
2. Assume that you could titrate to the third equivalence point of  $\text{H}_3\text{PO}_4$ . What would be the relationship of  $V_{\text{eq}3}$  to  $V_{\text{eq}2}$  and  $V_{\text{eq}1}$ ?
3. What is the structure of citric acid? Use a simple molecular diagram here.
4. How could  $\text{CO}_2$  interfere with the titration of  $\text{H}_3\text{PO}_4$ ?
5. The glass electrode that you used appears to be a single device, while it is actually two electrodes. Explain.

**Extension Activity:** Name \_\_\_\_\_

**Determination of acid content in soft drink**

*Purpose*

*Procedure*

Explain the procedure used to prepare the cola and uncola samples.

**Calculations**

A. Titration of NaOH and KHP

Concentration of KHP: \_\_\_\_\_ M

Volume of NaOH at equivalence point: \_\_\_\_\_ mL

Concentration of NaOH: \_\_\_\_\_ M

Plot pH vs. volume of NaOH for this titration. Use graph paper and label the equivalence point.

B. Data for titration of cola and uncola with NaOH

Make a table with the following columns:

Vol. NaOH Added	pH	$V_2 - V_1$	$\text{pH}_2 - \text{pH}_1$	$(V_1 + V_2)/2$	$\frac{\text{pH}_2 - \text{pH}_1}{V_2 - V_1}$
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Plot the first-derivative plots using the above data.

C. Results

Cola: volume of first equivalence point: \_\_\_\_\_ ml; pH: \_\_\_\_\_

volume of second equivalence point: \_\_\_\_\_ ml; pH: \_\_\_\_\_

molarity of  $\text{H}_3\text{PO}_4$ : \_\_\_\_\_ M; molarity of  $\text{H}_2\text{PO}_4^-$ : \_\_\_\_\_ M

Uncola: volume of equivalence point: \_\_\_\_\_ ml; pH: \_\_\_\_\_

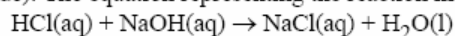
molarity of citric acid: \_\_\_\_\_ M

## Appendix 9 : Samples of Various Titration Curves – Teacher Support

Plotting the pH of the solution during an acid/base titration generates a “titration curve”. The general shape of the curves generated in a series of titrations may be grouped into families, according to the solution titrated and the titrating solutions. Typical examples of the general shapes are illustrated for four classes of titration:

**I: A solution of a strong acid titrated with a solution of a strong base.**

In this example 25.0 mL of 0.100 mol L<sup>-1</sup> aqueous solution of hydrochloric acid, HCl, (a monoprotic strong acid) is titrated with a 0.100 mol L<sup>-1</sup> aqueous solution of sodium hydroxide, NaOH(aq) (an ionic hydroxide). The equation representing the reaction may be written as:



or as the net ionic equation:  $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2 \text{H}_2\text{O(l)}$

At equivalence, moles HCl originally present = moles NaOH added

Volume HCl original × Concentration HCl solution = Volume NaOH added × Concentration NaOH solution

At equivalence,  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ ;  $[\text{Na}^+] = [\text{Cl}^-]$ ; and since Na<sup>+</sup> (aq) is a weaker acid than water and Cl<sup>-</sup> is a weaker base than water, the solution is described as “neutral”. At 25°C, the pH will be 7.0 (under the usual set of assumptions).

The expected titration curve is shown in figure 1 below.

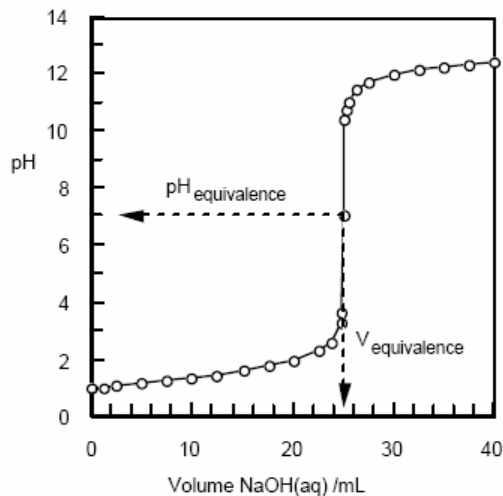


Figure 1: 0.1 M HCl(aq) vs. 0.1 M NaOH(aq)

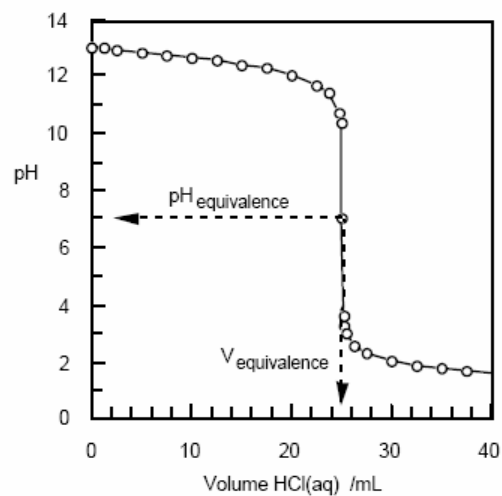


Figure 2: 0.1 M NaOH(aq) vs. 0.1 M HCl(aq)

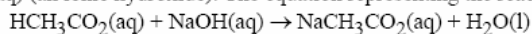
**II. A solution of a strong base with a solution of a strong acid.**

This is analogous to the strong acid/strong base titration except that the acid is the independent variable (*i.e.*, is added from a burette or equivalent). The example chosen is the titration of 25.0 mL of a 0.100 mol/L aqueous solution of sodium hydroxide with an 0.100 mol/L solution of hydrochloric acid. The expected titration curve is shown in figure 2 above.

For both cases I and II, the end point (assumed the equivalence point) is found at the steepest part of the curve, the inflection point where the curve changes direction.

**III. A solution of a weak acid with a solution of a strong base**

In this example 25.0 mL of 0.100 mol L<sup>-1</sup> aqueous solution of acetic acid, HCH<sub>3</sub>CO<sub>2</sub>, (a monoprotic weak acid with  $K_a = 1.8 \times 10^{-5}$  mol L<sup>-1</sup>) is titrated with a 0.100 mol L<sup>-1</sup> aqueous solution of sodium hydroxide, NaOH(aq) (an ionic hydroxide). The equation representing the reaction may be written as:



or as the net ionic equation:  $\text{HCH}_3\text{CO}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{CO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

(For a weak acid, the acid of highest concentration in an aqueous solution is the undissociated acid, not the hydronium ion.)

At equivalence, moles HCH<sub>3</sub>CO<sub>2</sub> originally present = moles NaOH added

At equivalence,  $[\text{HCH}_3\text{CO}_2] = [\text{OH}^-]$ ;  $[\text{Na}^+] = [\text{CH}_3\text{CO}_2^-]$ ; and since Na<sup>+</sup> (aq) is a weaker acid than water while CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> is a stronger base than water, the solution will be basic. At 25°C, the pH will be greater than 7.0 (under the usual set of assumptions).

The expected titration curve is shown in figure 3 below.

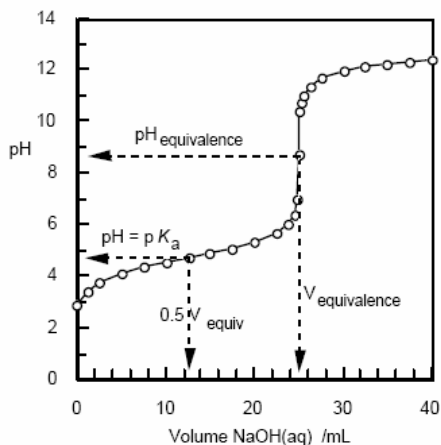


Figure 3: 0.1 M HOAc(aq) vs. 0.1 M NaOH(aq)

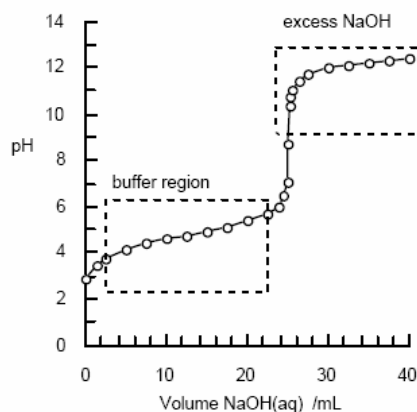


Figure 3(b)

The end point (assumed the equivalence point) is found at the steepest part of the curve, the inflection point where the curve changes direction.

In a titration of a weak acid with a strong base (or of a weak base with a strong acid, case IV), the region between about 10% and 90% of the equivalent volume added is described as the "buffer region" (Figure 3(b)). In this "region" both "undissociated" acid and its conjugate base (the anion) are present in appreciable concentrations, and the pH does not change appreciably as more hydroxide ion is added to the mixture. (A mixture of a weak acid and its conjugate base, or of a weak base and its conjugate acid, are the common descriptions for a buffer solution.)

At the half-equivalence volume ( $0.5 V_{\text{equivalence}}$ ),  $[\text{HCH}_3\text{CO}_2] = [\text{CH}_3\text{CO}_2^-]$ , and  $K_a = [\text{H}_3\text{O}^+]$ ; thus  $\text{pH} = \text{p}K_a$ .

#### IV. A solution of a weak base with a solution of a strong acid.

This is analogous to the weak acid/strong base titration except that the acid is the independent variable (*i.e.*, is added from a buret or equivalent). The example chosen is the titration of 25.0 mL of an 0.100 mol  $\text{L}^{-1}$  solution of aqueous ammonia ( $K_b = 1.8 \times 10^{-5} \text{ mol L}^{-1}$ ) with a 0.100 mol  $\text{L}^{-1}$  solution of hydrochloric acid. The expected titration curve is shown in figure 4 below.

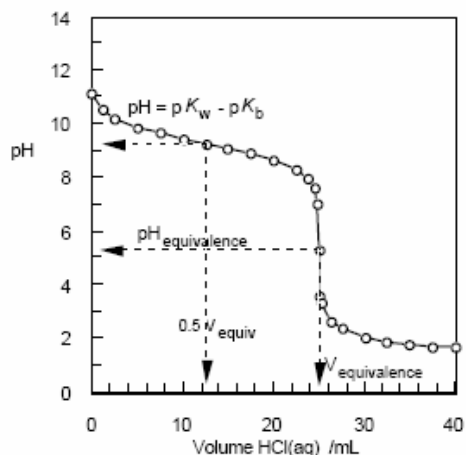


Figure 4: 0.1 M  $\text{NH}_3(\text{aq})$  vs. 0.1 M  $\text{HCl}(\text{aq})$

The end point (assumed the equivalence point) is found at the steepest part of the curve, the inflection point where the curve changes direction.

At the half-equivalence volume,  $[\text{NH}_4^+] = [\text{NH}_3]$ , and  $[\text{H}_3\text{O}^+] = K_a$  for the conjugate acid  $\text{NH}_4^+$ . Since, for a conjugate acid-base pair,  $K_a = K_w/K_b$ , at half-equivalence,  $\text{pH} = \text{p}K_w - \text{p}K_b$

#### Selecting an indicator

A suitable indicator of a titration should change color at the equivalence point of the titration. Indicators do not change abruptly but rather over a pH range. Some typical acid-base indicators are given in the table below:

Indicator	color change	pH range
bromocresol green	yellow → blue	3.6 – 5.2
methyl red	red → yellow	4.8 – 6.0
bromothymol blue	yellow → blue	6.0 – 7.6
phenol red	yellow → red	6.8 – 8.4
phenolphthalein	colorless → pink	8.0 – 9.8

For an effective end point, one drop (0.02 mL) of titrant should change the color of the indicator solution. Select an indicator which changes just past the equivalence point but still within the steepest portion of the titration curve. (You also need to be able to see the change – some people are color blind and don't recognize red-green changes for example, others have difficulty seeing changes like pink to colorless.)

For the model titrations shown, suitable indicators might include:

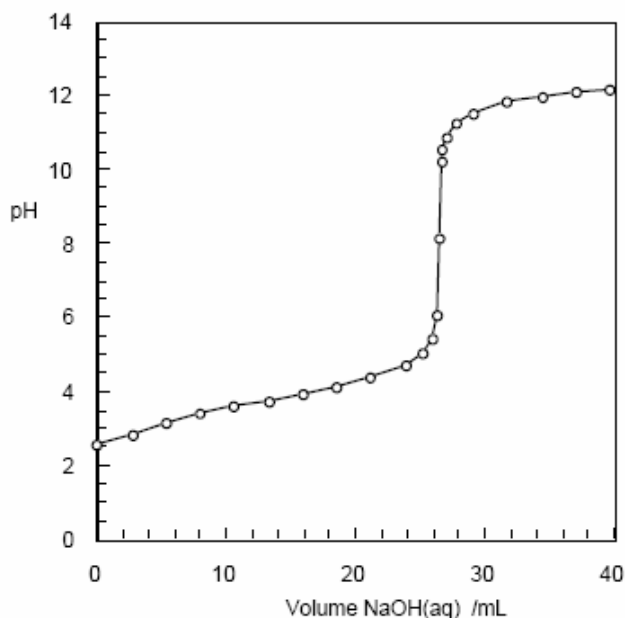
HCl vs. NaOH: any of bromothymol blue, phenol red, or phenolphthalein

NaOH vs. HCl: any of bromocresol green, methyl red, or bromothymol blue

HOAc vs. NaOH: phenolphthalein

NH<sub>3</sub> vs. HCl: methyl red or bromocresol green

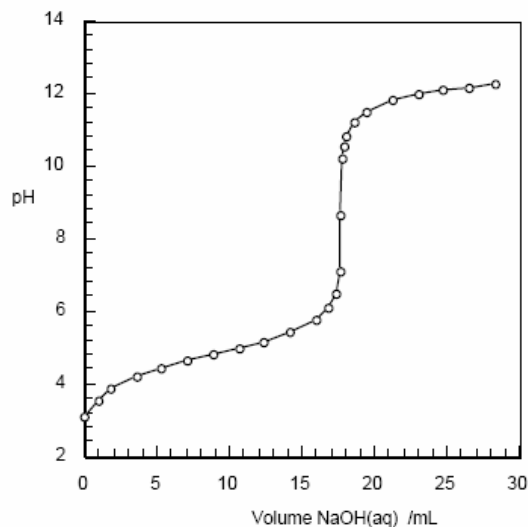
Note: It is beneficial to titrate both HCl vs. NaOH and NaOH vs. HCl with different indicators to better establish the neutral to basic and neutral to acid end point with one drop of indicator.



A student pipetted 25.0 mL of an aqueous solution of an unknown acid into a conical flask, added 25 mL of water, and then titrated the resulting mixture with a standard 0.0985 mol L<sup>-1</sup> solution of aqueous sodium hydroxide, measuring the pH of the mixture after each addition. The above graph shows the titration curve obtained.

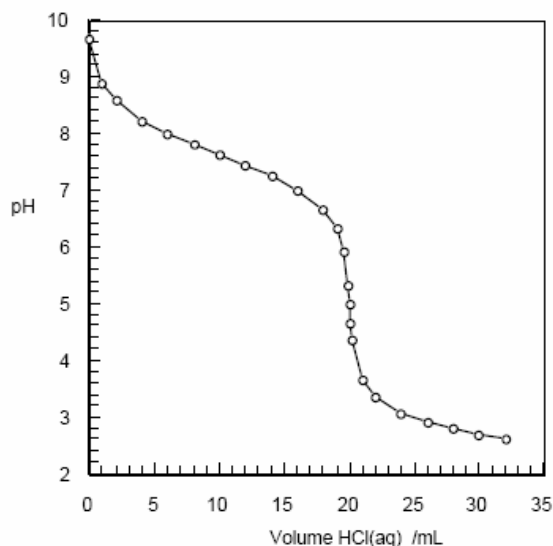
Using this graph, answer the following questions:

1. What was the concentration of the unknown acid solution?
2. What would be a suitable indicator for this solution?
3. Assuming the unknown acid is a weak monoprotic acid, estimate its  $K_a$  value.



A student weighed 0.225 g of a solid unknown acid into a conical flask, added about 50 mL of water, and then titrated the resulting mixture with a standard  $0.1245 \text{ mol L}^{-1}$  solution of aqueous sodium hydroxide, measuring the pH of the mixture after each addition. The above graph shows the titration curve obtained. Using this graph, answer the following questions:

1. What would be a suitable indicator for this solution?
2. Assuming the unknown acid is a weak monoprotic acid, estimate its  $K_a$  value.
3. Estimate the molar mass of the unknown acid.
4. Would the results obtained have been different if she had added 100 mL of water? Explain your answer.



A student weighed 0.0165 g of a solid unknown base into a conical flask, added about 100 mL of water, and then titrated the resulting mixture with a standard  $0.02635 \text{ mol L}^{-1}$  solution of hydrochloric acid, measuring the pH of the mixture after each addition. The above graph shows the titration curve obtained. Using this graph, answer the following questions:

1. What would be a suitable indicator for this solution?
2. Assuming the unknown base is a weak monoprotic base, estimate its  $K_b$  value. Estimate the  $K_a$  of its conjugate acid.
3. Estimate the molar mass of the unknown base.

