

TOPIC 5: ACIDS AND BASES

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Appendix 5.1: Selected Neutralization Indicators

Indicator	Colour Change (lower pH listed first)	Approximate pH (range of colour change)
Methyl violet	Yellow to blue	0.0 to 1.6
Crystal violet	Yellow to violet	0.1 to 1.6
Paramethyl red	Red to yellow	1.0 to 3.0
Methyl yellow	Red to yellow	2.9 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
Bromcresol purple	Yellow to purple	5.2 to 6.8
Litmus	Red to blue	5.5 to 8.0
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
Phenolphthalein	Colourless to pink	8.3 to 10.0
Thymolphthalein	Colourless to blue	9.4 to 10.6
Alizarin yellow	Yellow to red	10.0 to 12.0
Alizarin blue-5	Amber and green to blue-green	11.0 to 12.0

Appendix 5.2: Acid-Base Indicators and pH: Lab Activity

Introduction

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 that 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 that has been soaked in a solution of dye(s) called indicator(s). The 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 activity, three individual indicators (methyl orange, phenolphthalein, and bromothymol blue) and a standard mixture of indicators (universal) will be used. The standard universal indicator is a mixture of organic dyes that change colour and allow for a fairly accurate approximation of the whole number pH value of a test solution.

Purpose

To develop an operational definition of pH.

Materials and Apparatus

well plate
white paper
eyedroppers
distilled water
0.1 mol/L hydrochloric acid (HCl)
0.1 mol/L sodium hydroxide (NaOH)
universal indicator
methyl orange indicator
phenolphthalein indicator
bromothymol blue indicator

Appendix 5.2: Acid-Base Indicators and pH: Lab Activity *(continued)*

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 eyedropper and then returning the liquid to well A2.
5. Transfer 1 drop from well A2 to well A3, again mixing by drawing the contents of well A3 into an eyedropper and returning the contents to well A3. Continue the serial dilution in this manner through to 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 A11 into an eyedropper and then returning the liquid to well A11.
8. Now transfer 1 drop from well A11 to well A10, again mixing by drawing the contents of well A10 into an eyedropper and returning the contents to well A10. Continue the serial dilution in this manner backwards through to 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 1/10th of the acid of the well to its left and 1/10th of 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 bromothymol 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 an HCl/NaOH titration? Why?
4. Which would be a poor indicator for an HCl/NaOH titration? Why?

Appendix 5.3A: Measuring pH: Lab Activity

Introduction

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

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

An acid-base indicator is a substance whose colour in solution depends upon the hydronium ion concentration. Acid-base indicators change colour from their acid form to their base form over a specific range of pH.

Purpose

To determine the colours 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 colour 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 aqueous hydrochloric acid ($\text{HCl}_{(\text{aq})}$) solution in well 1 of rows A, C, E, and G.
4. Place 10 drops of a 0.1 mol/L aqueous sodium hydroxide (NaOH) solution in well 12 of rows A, C, E, and G.
5. Transfer 1 drop of 0.1 mol/L $\text{HCl}_{(\text{aq})}$ solution from well A1 to well A2. Mix thoroughly by stirring with a new toothpick or a 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 1 drop from well A2 to well A3, 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.

Appendix 5.3A: Measuring pH: Lab Activity *(continued)*

7. Repeat the dilution procedure using the 0.1 mol/L NaOH_(aq) solution in the same rows as the acid dilution, working backwards from well 12 to well 8, making well 8 the last basic dilution. You now have 4 rows each of the 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 that 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 colour change.
14. Describe how you could use the results from this experiment to estimate the pH of an aqueous solution.

Appendix 5.3B: Measuring pH: Lab Activity (Teacher Notes)

Preparation of Indicator Solutions

These solutions can be prepared in advance and remain stable for at least six months.

- **Methyl orange**

Dissolve 0.01 g of methyl orange in 100 mL of distilled water.

- **Bromothymol blue**

Dissolve 0.04 g of the sodium salt of bromothymol blue in 100 mL of distilled water.

- **Phenolphthalein**

Dissolve 0.05 g of phenolphthalein 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 aqueous sodium hydroxide solution until the mixture is green, and dilute the resulting solution to 100 mL with distilled water.

Appendix 5.4: Relative Strengths of Acids

Acid	Reaction	K_a
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
Sulphuric 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	$\text{HOOC-COOH} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HOOC-COO}^-$	5.4×10^{-2}
Sulphurous acid	$\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_3^-$	1.7×10^{-2}
Hydrogen sulphate ion	$\text{HSO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$	1.3×10^{-2}
Phosphoric acid	$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$	7.1×10^{-3}
Ferric ion	$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	6.0×10^{-3}
Hydrogen telluride	$\text{H}_2\text{Te} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HTe}^-$	2.3×10^{-3}
Hydrofluoric acid	$\text{HF} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{F}^-$	6.7×10^{-4}
Nitrous acid	$\text{HNO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_2^-$	5.1×10^{-4}
Hydrogen selenide	$\text{H}_2\text{Se} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSe}^-$	1.7×10^{-4}
Chromic ion	$\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	1.5×10^{-4}
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{COO}^-$	6.6×10^{-5}
Hydrogen oxalate ion	$\text{HOOC-COO}^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OOC-COO}^{2-}$	5.4×10^{-5}
Acetic acid	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	1.8×10^{-5}
Aluminum ion	$\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	1.4×10^{-5}
Carbonic acid	$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^-$	4.4×10^{-7}
Hydrogen sulphide	$\text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HS}^-$	1.0×10^{-7}
Dihydrogen phosphate ion	$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$	6.3×10^{-8}
Hydrogen sulphite ion	$\text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SO}_3^{2-}$	6.2×10^{-8}
Ammonium ion	$\text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NH}_3$	5.7×10^{-10}
Hydrogen carbonate ion	$\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-}$	4.7×10^{-11}
Hydrogen telluride ion	$\text{HTe}^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Te}^{2-}$	1.0×10^{-11}
Hydrogen peroxide	$\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HO}_2^-$	2.4×10^{-12}
Monohydrogen phosphate ion	$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{PO}_4^{3-}$	4.4×10^{-13}
Hydrogen sulphide ion	$\text{HS}^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{S}^{2-}$	1.2×10^{-15}
Water	$\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$	1.8×10^{-16}
Hydroxide ion	$\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{O}^{2-}$	$< 10^{-36}$
Ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NH}_2^-$	Very small

Appendix 5.5: Quantitative Analysis: Acid-Base Titration: Lab Activity

Purpose

In this lab activity, students will do the following:

- Standardize a base solution using a stock acid solution by the method of titration.
- Given an unknown mass of a solid acid, 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

1. Obtain two burettes, placing one on the left for the acid and the other on the right for the base. Before using the burettes, carefully wash them with soap and water, and then rinse them with tap water to remove all soap. Then rinse the burettes with 15 mL portions of distilled water, ensuring there are no air bubbles in the tips of the burettes. Finally, rinse the burettes with several small (10 to 15 mL) aliquots of each solution.
2. Fill one burette with the acid and the other with the base. To determine the initial acid and base volumes, read each burette to the nearest 0.01 mL.
3. Introduce about 10 to 15 mL of acid 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 burette and record it as the final acid reading. Add about three drops of phenolphthalein indicator to the flask. Use a clean flask for each trial.
4. While continuously swirling the flask, slowly add the base until a pale lasting pink colour persists, indicating the end point.
Note: As the end point is approached, the colour disappears more slowly until finally the pale pink colour persists. Then carefully read the volume from the base burette and record it as the final base volume.
5. Repeat this entire process as many times (minimum 4) as needed to obtain consistency of data to three significant figures for the base concentration.
6. Select the three best trials and record them in a Data Table. Show calculations for each trial. Calculate the average of the three trials. Record this average.

Appendix 5.5: Quantitative Analysis: Acid-Base Titration: Lab Activity (continued)

Part B

1. Obtain a vial containing a sample of sulphamic acid with the formula $\text{H}_2\text{NSO}_3\text{H}$ and a molar mass of 97.09 g/mol.
2. Transfer the solid acid to a 100 mL volumetric flask. Fill half the flask with water and swirl until the solid dissolves completely, and then fill the flask with water exactly to the 100 mL mark. Take great care with the acid sample, as only one sample will be handed out per student. The 100 mL sample is enough for five to eight titrations, which should be enough to complete the determination.
3. Once the acid solution has been prepared, follow the procedure used for Part A of this experiment. This time, however, use the sulphamic acid instead of the hydrochloric acid and a new standard base stock solution. The concentration of the base can be read off the stock solution.
4. Select three of the best trials and record them in a Data Table. Calculate the mass to 0.001 g.

Calculations and Questions

1. Record the values of the acid and base volumes from Part A in the Titration Data Table provided on the following page.
2. Calculate the concentration of the base used. Show all work.
3. Record the values of the acid and base values from Part B in the Titration Data Table provided.
4. Calculate the concentration of the sulphamic acid in the sample. Show all work.
5. Calculate the mass of the sample of sulphamic acid. Present the average of the best three trials. Show all work.
6. 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 $[\text{OH}^-]$?
7. What would you expect the pH of the solution to be just at the point at which the phenolphthalein turns pink?
8. Why is an indicator solution so important to use for titrations?
9. What does the following statement mean? "The relative volumes required in a titration vary inversely with the concentrations of the solutions."

Appendix 5.5: Quantitative Analysis: Acid-Base Titration: Lab Activity (continued)

Titration Data Table (Part A)			
Trial	Burette Reading	Acid	Base
1	Final burette reading		
	Initial burette reading		
	Total volume		
2	Final burette reading		
	Initial burette reading		
	Total volume		
3	Final burette reading		
	Initial burette reading		
	Total volume		
4	Final burette reading		
	Initial burette reading		
	Total volume		
5	Final burette reading		
	Initial burette reading		
	Total volume		
6	Final burette reading		
	Initial burette reading		
	Total volume		
7	Final burette reading		
	Initial burette reading		
	Total volume		
8	Final burette reading		
	Initial burette reading		
	Total volume		

Appendix 5.5: Quantitative Analysis: Acid-Base Titration: Lab Activity (continued)

Titration Data Table (Part B)			
Trial	Burette Reading	Acid	Base
1	Final burette reading		
	Initial burette reading		
	Total volume		
2	Final burette reading		
	Initial burette reading		
	Total volume		
3	Final burette reading		
	Initial burette reading		
	Total volume		
4	Final burette reading		
	Initial burette reading		
	Total volume		
5	Final burette reading		
	Initial burette reading		
	Total volume		
6	Final burette reading		
	Initial burette reading		
	Total volume		
7	Final burette reading		
	Initial burette reading		
	Total volume		
8	Final burette reading		
	Initial burette reading		
	Total volume		

Appendix 5.6: Analysis of Household Vinegar: Lab Activity

Purpose

To determine the percent of 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 contain 5% acetic acid.

Procedure

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

Data Table

		Trial 1	Trial 2	Trial 3
Burette reading	Final reading			
	Initial reading			
	Volume used			
Concentration of standardized NaOH				

Appendix 5.6: Analysis of Household Vinegar: Lab Activity *(continued)*

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

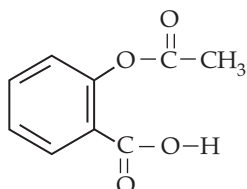
Mass of $\text{HC}_2\text{H}_3\text{O}_2$ in sample:

Percent of $\text{HC}_2\text{H}_3\text{O}_2$ by mass:

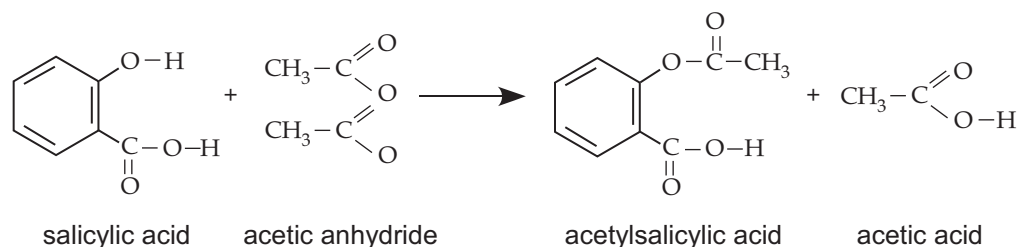
Appendix 5.7: Analysis of Aspirin: Lab Activity

Introduction

Acetylsalicylic acid, sometimes abbreviated as ASA, is the active ingredient in Aspirin. The structural formula of ASA is given below.



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

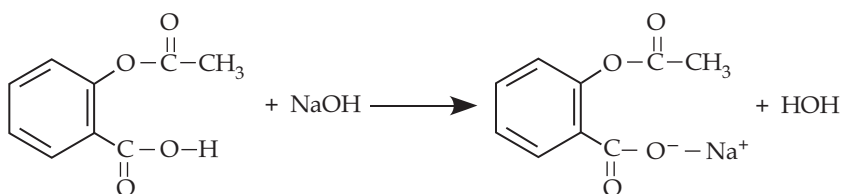


The product is removed from the reaction mixture by crystallization. The crude ASA must be purified by washing to remove excess by-products and then re-crystallized in the pure state.

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

Purpose

The purpose of this analysis is to determine the degree of purity of various commercial ASA products. The analysis is based on titration of the ASA tablets 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 end point is reached, as indicated by the phenolphthalein indicator. The percent of ASA present can then be calculated.

Appendix 5.7: Analysis of Aspirin: Lab Activity *(continued)*

Procedure

1. Determine the mass of a single ASA tablet to the nearest 0.01 g by direct weighing.
2. 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 the solution to dissolve the tablet. Complete solution may not be accomplished prior to titration with the base solution.
3. Add approximately three drops of phenolphthalein indicator solution. No colour change should be seen.
4. Carefully fill a 50 mL burette with standard 0.1 mol/L sodium hydroxide solution. Record the exact concentration of the standard sodium hydroxide solution.
5. Record the level of sodium hydroxide solution in the burette. Place the flask containing the ASA sample under the burette.
6. Add small volumes of sodium hydroxide solution, while swirling the flask. Continue adding sodium hydroxide solution until the first indication that a phenolphthalein end point has been reached, as indicated by a light pink colour throughout the solution in the flask. This colour should remain without fading upon swirling.
7. Record the level of the solution in the burette.

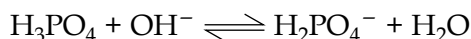
Calculations

Calculate the percent of ASA in your tablet. The formula mass of ASA is 180 g/mol, and each molecule transfers 1 hydrogen ion to a base.

Appendix 5.8: Potentiometric Analysis of Acid in Soft Drinks: Cola versus Non-cola: Lab Activity

Introduction

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 flavours. There is some variability in both the amount and composition of the acid in cola drinks. The composition is affected by the equilibrium



Purpose

In this experiment, you will determine the H_3PO_4 and H_2PO_4^- in a sample of cola drink using a potentiometric titration. A potentiometric detection method is preferred over an acid-base indicator for two reasons:

- The colour of the cola obscures indicator changes.
- The use of a pH meter permits a more accurate location of the equivalence points in a titration than an indicator.

You will also determine the citric acid concentration in a non-cola drink. Citric acid, which is also tri-basic, is another common ingredient in many soft drinks. The acid dissociation constants for phosphoric and citric acids are as follows:

Dissociation Constant	Phosphoric Acid	Citric Acid
K_1	7.11×10^{-3}	7.44×10^{-4}
K_2	6.32×10^{-8}	1.73×10^{-5}
K_3	7.10×10^{-13}	4.02×10^{-7}

From these data, it is clear that the constants for phosphoric acid are more than a factor of 1000 apart, and three distinct end points 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 end points. Moreover, several of the citric and phosphoric acid end points are close, so it is advisable to carry out this experiment with soft drinks that do not contain both phosphoric and citric acid. A possible choice is using Coca-Cola for the phosphoric acid determination, and Squirt for the citric acid determination. If you choose other brands, read the list of ingredients to make sure that only one or the other of the acids is present. The drinks also should not contain lactic acid or aspartame (e.g., NutraSweet), so do not choose diet drinks.

**Appendix 5.8: Potentiometric Analysis of Acid in Soft Drinks:
Cola versus Non-cola: Lab Activity (continued)**

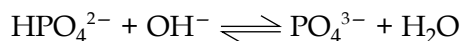
The potentiometric response of the glass electrode is described by the equation

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

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 H_3PO_4 solution is easily followed as a function of added NaOH.

At pH 10.5 to 11, the glass electrode begins to respond to other ions (mainly Na^+ in this case) since so few H_3O^+ 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:

**Pre-laboratory Assignment**

The phosphoric acid in a 100 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 was added, calculate the concentrations of H_3PO_4 and H_2PO_4^- in the cola sample. (**Hint:** Where would the second equivalence point have occurred if only H_3PO_4 were present?)

Apparatus

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

**Appendix 5.8: Potentiometric Analysis of Acid in Soft Drinks:
Cola versus Non-cola: Lab Activity (continued)**

Chemicals

sodium hydroxide
primary standard – potassium hydrogen phthalate (KHP)
cola unknown (e.g., Coca-Cola)
non-cola unknown (e.g., Squirt)
pH 4 and 7 buffers
phenolphthalein indicator

Procedure

1. Standardize the pH meter with the buffers.
2. Prepare a standard 0.10 N NaOH solution (using a KHP primary standard). For the titration, use the pH electrode in conjunction with the phenolphthalein indicator and compare the electrode response to the indicator colour 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 versus volume of titrant), you need to proceed somewhat beyond the equivalence point. The electrode response will be the principal indicator of the end point in this experiment, but you should observe that the indicator changes colour 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 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 will expel the CO₂ which otherwise would interfere with the titration of H₃PO₄. 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 burette 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 to 6 with the non-cola. Now only one equivalence point should be found, near pH 6.

**Appendix 5.8: Potentiometric Analysis of Acid in Soft Drinks:
Cola versus Non-cola: Lab Activity (continued)**

Calculations

1. Plot pH (ordinate, i.e., y -axis) versus 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 $(\text{pH}_2 - \text{pH}_1)/(V_2 - V_1)$ versus $(V_1 + V_2)/2$, where V_1 and V_2 are two successive titration volumes (totals) and pH_1 and 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 H_3PO_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 $V_{\text{eq}2} > 2V_{\text{eq}1}$, then not only H_3PO_4 but also H_2PO_4^- was present in the drink (see Pre-laboratory Assignment). Calculate the concentrations of both.
5. Calculate the concentration of citric acid in the non-cola.

Questions

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 H_3PO_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? Draw a simple molecular diagram.
4. How could CO_2 interfere with the titration of H_3PO_4 ?
5. The glass electrode that you used appears to be a single device, while it is actually two electrodes. Explain.

Appendix 5.8: Potentiometric Analysis of Acid in Soft Drinks: Cola versus Non-cola: Lab Activity (continued)

Extension Activity

Determination of acid in soft drink

Purpose

Specify the purpose.

Procedure

Explain the procedure used to prepare the cola and non-cola samples.

Calculations

A. Titration of NaOH and KHP

Concentration of KHP: _____ mol/L

Volume of NaOH at equivalence point: _____ mL

Concentration of NaOH: _____ mol/L

Plot pH versus volume of NaOH for this titration, using graph paper. Label the equivalence point.

B. Data for titration of cola and non-cola with NaOH

Make a data table with the following columns:

Data Table

Vol. NaOH Added	pH	$V_2 - V_1$	$\text{pH}_2 - \text{pH}_1$	$\frac{(V_1 + V_2)}{2}$	$\frac{\text{pH}_2 - \text{pH}_1}{V_2 - V_1}$
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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 H_3PO_4 : _____ mol/L

Molarity of H_2PO_4^- : _____ mol/L

Non-cola: Volume of equivalence point: _____ mL pH: _____

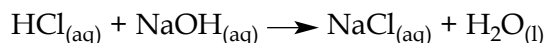
Molarity of citric acid: _____ mol/L

Appendix 5.9: Samples of Various Titration Curves (Teacher Notes)

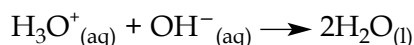
Plotting the pH of the solution during an acid-base titration generates a titration curve. The general shape of the curves generated in a series of titrations may be grouped into families, according to the solution titrated and the titrating solutions. Typical examples of the general shapes for four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

1. A Solution of a Strong Acid Titrated with a Solution of a Strong Base

In this example, 25.0 mL of a 0.100 mol/L aqueous solution of hydrochloric acid, HCl (a monoprotic strong acid), is titrated with a 0.100 mol/L 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



At equivalence, moles HCl originally present = moles NaOH added.

Volume HCl original \times concentration HCl solution = Volume NaOH added \times concentration NaOH solution.

At equivalence, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ and $[\text{Na}^+] = [\text{Cl}^-]$. Since Na⁺_(aq) is a weaker acid than water and Cl⁻ 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.

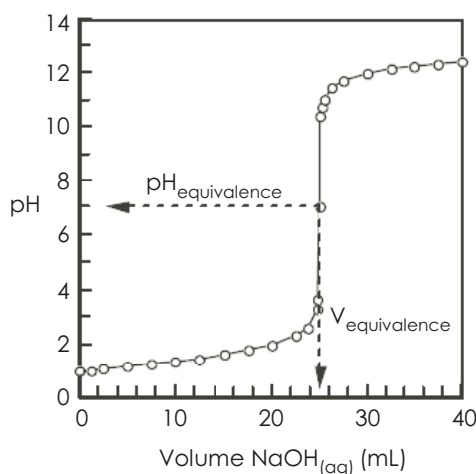


Figure 1: 0.1 mol/L HCl_(aq) versus 0.1 mol/L NaOH_(aq)

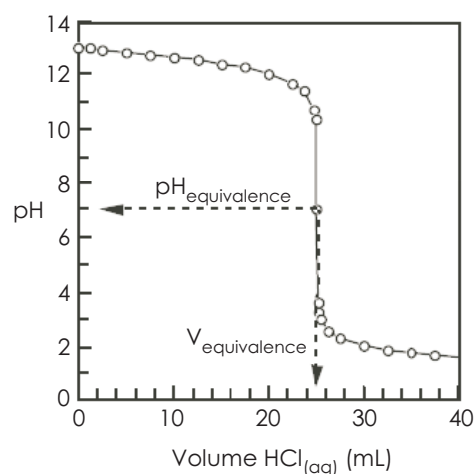


Figure 2: 0.1 mol/L NaOH_(aq) versus 0.1 mol/L HCl_(aq)

Appendix 5.9: Samples of Various Titration Curves (continued)

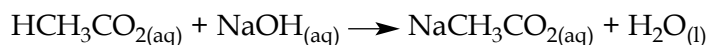
2. A Solution of a Strong Base Titrated with a Solution of a Strong Acid

This titration is analogous to the strong acid and 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 a 0.100 mol/L solution of hydrochloric acid. The expected titration curve is shown in Figure 2 on the previous page.

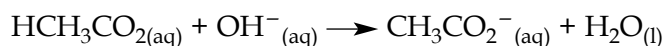
For both examples 1 and 2, the end point (assumed the equivalence point) is found at the steepest part of the curve, the inflection point where the curve changes direction.

3. A Solution of a Weak Acid Titrated with a Solution of a Strong Base

In this example, 25 mL of a 0.100 mol/L aqueous solution of acetic acid, HCH_3CO_2 (a monoprotic weak acid with $K_a = 1.8 \times 10^{-5}$ mol/L), is titrated with a 0.100 mol/L aqueous solution of sodium hydroxide, $\text{NaOH}_{(\text{aq})}$ (an ionic hydroxide). The equation representing the reaction may be written as



or as the net ionic equation



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_3CO_2 originally present = moles NaOH added.

At equivalence, $[\text{HCH}_3\text{CO}_2] = [\text{OH}^-]$ and $[\text{NA}^+] = [\text{CH}_3\text{CO}_2^-]$. Since $\text{NA}^+_{(\text{aq})}$ is a weaker acid than water and CH_3CO_2^- 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).

Appendix 5.9: Samples of Various Titration Curves (continued)

The expected titration curve is shown in Figure 3a below.

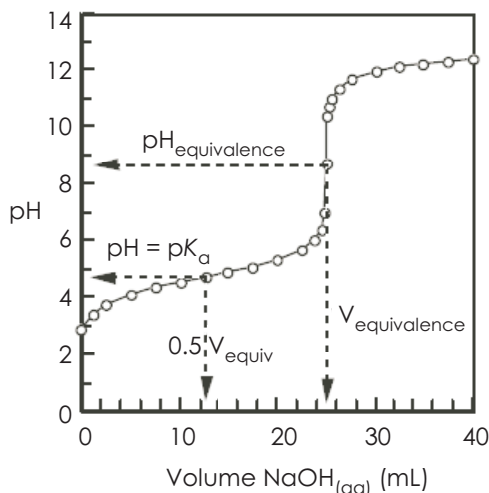


Figure 3a: 0.1 mol/L HOAc_(aq) versus
0.1 mol/L NaOH_(aq)

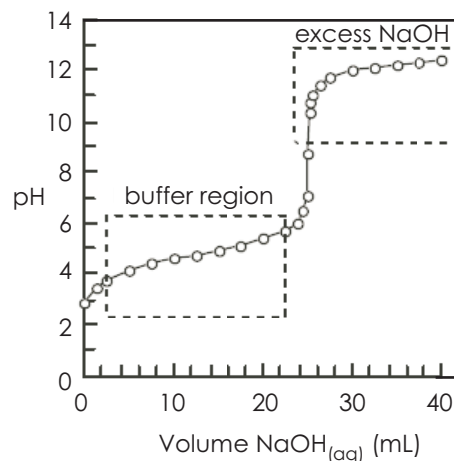


Figure 3b: 0.1 mol/L HOAc_(aq) versus
0.1 mol/L NaOH_(aq)

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

In a titration of a weak acid with a strong base (or of a weak base with a strong acid, example 4), the region between about 10% and 90% of the equivalence volume added is described as the *buffer region* (Figure 3b). 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, $\text{pH} = \text{p}K_a$.

Appendix 5.9: Samples of Various Titration Curves (continued)

4. A Solution of a Weak Base Titrated with a Solution of a Strong Acid

This titration is analogous to the weak acid and 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 solution of aqueous ammonia ($K_b = 1.8 \times 10^{-5}$ mol/L) with a 0.100 mol/L solution of hydrochloric acid. The expected titration curve is shown in Figure 4 below.

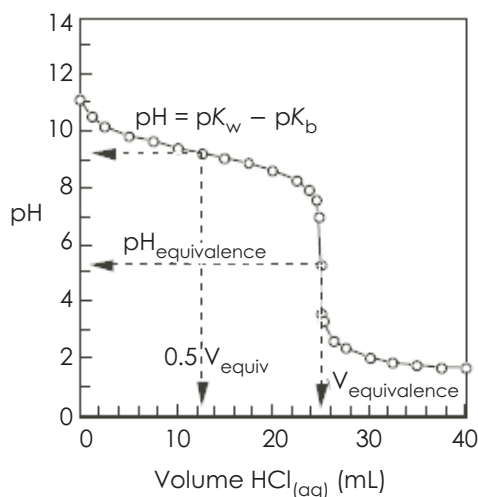


Figure 4: 0.1 mol/L $\text{NH}_3(\text{aq})$ versus
0.1 mol/L $\text{HCl}(\text{aq})$

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 NH_4^+ . Since, for a conjugate acid-base pair, $K_a = K_w/K_b$, at half-equivalence, $\text{pH} = \text{p}K_w - \text{p}K_b$.

Appendix 5.9: Samples of Various Titration Curves (continued)

Selecting an Indicator

A suitable indicator of a titration should change colour 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.

Acid-Base Indicators		
Indicator	Colour 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	Colourless → pink	8.0 – 9.8

For an effective end point, one drop (0.02 mL) of titrant should change the colour of the indicator solution. Select an indicator that 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 colour blind and don't recognize red-green changes, for example, and others have difficulty seeing changes such as pink to colourless.)

For the model titrations shown, suitable indicators might include the following:

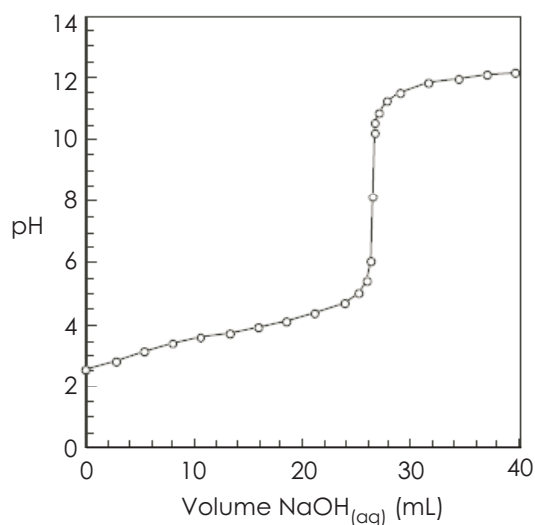
- HCl versus NaOH: any bromothymol blue, phenol red, or phenolphthalein
- NaOH versus HCl: any of bromocresol green, methyl red, or bromothymol blue
- HOAc versus NaOH: phenolphthalein
- NH₃ versus HCl: methyl red or bromocresol green

Note: For accuracy, it is beneficial to titrate both HCl versus NaOH and NaOH versus HCl with different indicators.

Appendix 5.9: Samples of Various Titration Curves (continued)

Learning Activity 1

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



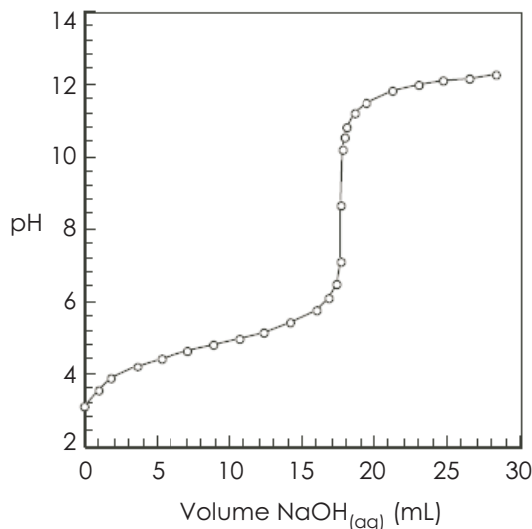
Using this graph, answer the following questions:

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.

Appendix 5.9: Samples of Various Titration Curves (continued)

Learning Activity 2

A student weighed 0.225 g of a solid unknown acid into a conical flask, added about 50.0 mL of water, and then titrated the resulting mixture with a standard 0.1245 mol/L solution of aqueous sodium hydroxide, measuring the pH of the mixture after each addition. The following graph shows the titration curve obtained.



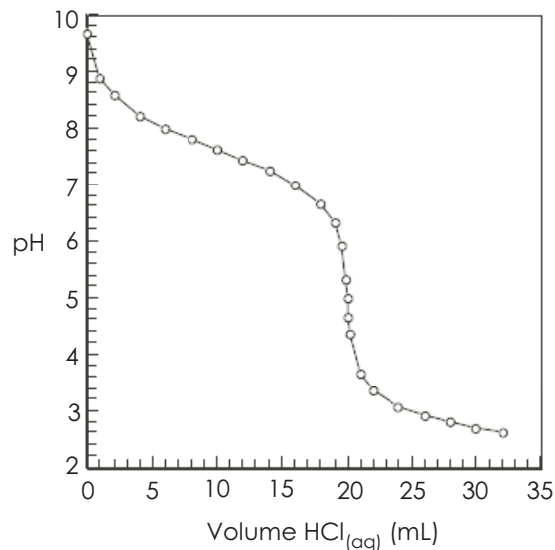
Using this graph, answer the following questions:

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 the student had added 100 mL of water? Explain.

Appendix 5.9: Samples of Various Titration Curves (continued)

Learning Activity 3

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 mol/L solution of hydrochloric acid, measuring the pH of the mixture after each addition. The following 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.