Experiment 4: Potentiometric Acid-Base Titrations

What lab skills will you practice?

- Performing acid-base titrations
- Determining the identity of an unknown acid
- Calibrating and using a pH meter

What chemical concepts will you apply?

- Dilutions — Silberberg: Chapter 3.5
- Neutralization — Silberberg: Chapter 17.2
- pK_a and pH — Silberberg: Chapter 16.1

What report writing skills will you use?

- Using a potentiometric titration curve to determine the endpoint of a titration
- Writing a complete formal lab report

Reminder:

- Complete the online pre-lab quiz at least 1hour before lab
- Have your 'blue book' prepared with data tables
- Print & bring Experiment 4 and Appendix I to lab

Objective

Using a potentiometric titration, determine the identity and concentration of an unknown weak monoprotic acid. Describe the properties of potentiometric titration curves, and the effect of the weak acid concentration on them.

Introduction

In this experiment, you will use both *qualitative* and *quantitative* properties to identify an unknown acid's composition and concentration. To do this analysis, you will perform a titration of your unknown acid sample – specifically a *potentiometric titration* where you use a pH meter and record pH values during the titration, combined with a *visual titration* using a color indicator to show the progress of the reaction. By titrating the sample at two different concentrations, you will also be able to compare the changes caused by the concentration change, and compare the effectiveness of the two titrations.

Acid-base Titrations

In Experiment 1, you performed a *complexometric titration*, involving the reaction between metal ions and EDTA, a complexing agent. In this experiment, we are performing an acid-base titration, where the reaction involved is a *neutralization reaction.*

Neutralization of a weak acid "HA": $HA + OH^- \longrightarrow A^- + H_2O$

Neutralization is a good type of reaction to use in a titration because it is *fast* and it has a *large equilibrium constant (K)*, so that the reaction will proceed nearly to "completion" – at each step, we can assume that all of the available reactants are consumed.

Although the reactants are different in an acid-base reaction, many of the basic principles are the same as the complexometric titration. However, since these titrations involve a change in pH during the reaction, we can use pH probes to monitor the reaction in a **potentiometric titration**.

Titration Curves

In a potentiometric titration, we will plot the pH of the analyte against the amount of titrant added. By using a pH probe to monitor the acidity of the solution, we can determine the endpoint without relying on a color indicator. A typical plot of pH vs. mL of titrant added for the titration of a weak acid is shown in Figure 1, highlighting some useful regions on the titration curve. All of the points described below will also exist for the titration of a weak base (by strong acid) – but you will only perform the titration of a weak acid in this experiment.

A. **Initial pH**: Before any titrant is added, the pH is determined only by the dissociation of weak acid present in solution.

B. **Buffer region**: Once some titrant is added, there will be weak acid as well as significant amounts of its conjugate base present in the flask. This creates a *buffer* – notice that the pH changes slowly as titrant is added in this region.

C. **Equivalence point**: At this point, exactly enough strong base has been added to react with all of the weak acid in solution, producing its conjugate base. Although the weak acid has been neutralized, the *pH is not always 7 at the equivalence point*. The reaction of the conjugate base with water determines the pH at the equivalence point.

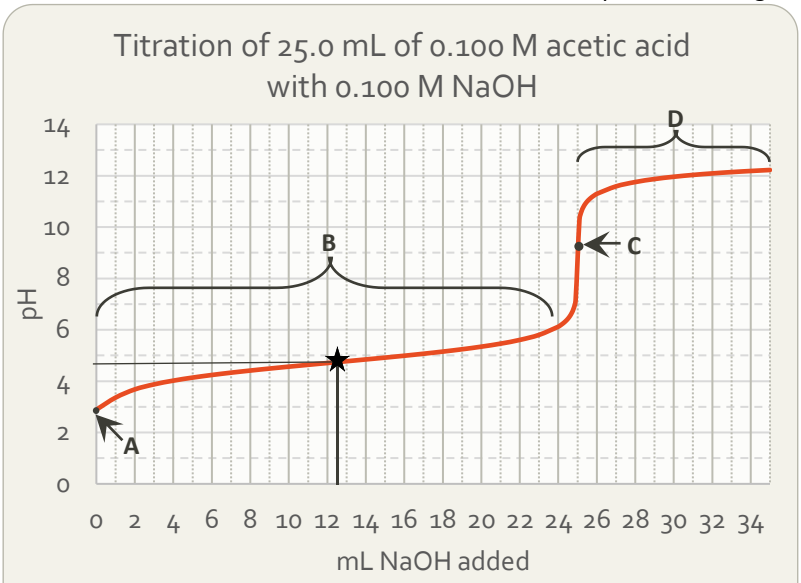

FIGURE 1: WEAK ACID - STRONG BASE TITRATION CURVE

D. **Beyond the equivalence point**: More titrant has been added than is needed to react with the analyte – there is excess OH^- in solution. The amount of excess OH^- in solution determines the pH beyond the equivalence point.

The point on the titration curve marked with a star (☆) is called the **half-equivalence point** – the point where enough base has been added to react with exactly half of the weak acid in the flask.

The Half-Equivalence Point

The half-equivalence point is especially useful in identifying weak acids, since it allows us to determine the acid's pK_a. At this point, exactly **half** the amount of base needed to neutralize the total amount of weak acid has been added – in other words:

mol OH^- added = ½ mol "HA" in flask

The OH^- added will react with the weak acid, resulting in a solution that contains an equal amount of the weak acid ("HA") and its conjugate base (A^-). We can prove this using the titration in Figure 1 as an example:

Amount of acetic acid:

$25.0\ mL \times 0.100\ M = 25.0\ mmol\ acetic\ acid$

Amount of OH^- needed to reach half-equivalence point:

$25.0\ mmol \div 2 = 12.5\ mmol\ OH^-\ needed$

$12.5\ mmol\ OH^- \div 0.100\ M = 12.5\ mL\ OH^-\ needed$

We can also read the equivalence point and half-equivalence point from the titration curve.

Neutralization of the weak acid: *(using HA = acetic acid and A^- = acetate)*

Reaction:	**HA**	**+**	**OH^-**	**→**	**A^-**	**+**	**H_2O**
Initial (mmol)	25.0		12.5		0		---
Change (mmol):	-12.5		-12.5		+12.5		---
Final (mmol):	12.5		0		12.5		---
Final (M):	0.333		0		0.333		---

React all of the OH^- if possible.

Remember: the total volume of solution after the reaction is: (25 + 12.5) = 37.5 mL

Since exactly half of the weak acid was neutralized, we are left with a solution containing equal amounts of unreacted weak acid and conjugate base. If we use the Henderson-Hasselbach relation to predict the pH of this mixture:

$$pH = pK_a + log\left(\frac{[A^-]}{[HA]}\right)$$

Since $[A^-] = [HA]$, $\frac{[A^-]}{[HA]} = 1$

$$pH = pK_a + log(1)$$

$$pH = pK_a$$

So – no matter what the original concentrations were, **at the half-equivalence point, pH = pK_a**. This relation can be useful when identifying an acid in a titration – if you can identify the half-equivalence point on the titration curve, the pH at that point will be the pK_a. In Figure 1, by reading the pH at the half-equivalence point (marked with a star) we can determine the pK_a to be approximately 4.75, which agrees with the pK_a of acetic acid.

Finding the Equivalence Point and Endpoint

Whether we determine it potentiometrically or with a color indicator, we assume that the endpoint occurs as near as possible to the equivalence point. This assumption depends on the choice of a color indicator that changes color as close as possible to the endpoint or, for a potentiometric titration, that the endpoint can be correctly read from the titration curve.

Visual titrations (with color indicators)

In visual titrations, the *first persistent color change* is taken as the endpoint. What color change this is depends on the indicator chosen – for example in the titration of an acid using a phenolphthalein indicator (color change from clear to pink), the first hint of pale pink that lasts several seconds without fading is the endpoint.

Potentiometric titrations (with a pH probe)

In a potentiometric (pH) titration, the pH is monitored as titrant is added, and the resulting titration curve is used to mathematically determine the endpoint. In these titrations, titrant is added well past the amount needed to reach the equivalence point in order to have the most accurate determination. The potentiometric endpoint will be in the *center of the region of rapid pH change* on the titration curve. This can be located mathematically or graphically – in this lab, we will use a graphical method to determine the potentiometric endpoint:

Finding an Endpoint Graphically

After plotting your data, draw two straight lines that incorporate as many data points as possible: One through the buffer region and one through the "excess titrant" region. (These lines are shown in red in Figure 2). Draw a third line through the region of greatest pH change, again including as many data points as possible. (This line is in blue in Figure 2).

The potentiometric endpoint lies at the midway point between the two intersections (halfway between "A" and "B" along the blue line in Figure 2). Read straight across to find the pH and straight down from this point to find the volume of titrant needed to reach the endpoint.

Since they are different methods of detecting the endpoint, the potentiometric endpoint and visual endpoint may not agree exactly for a titration.

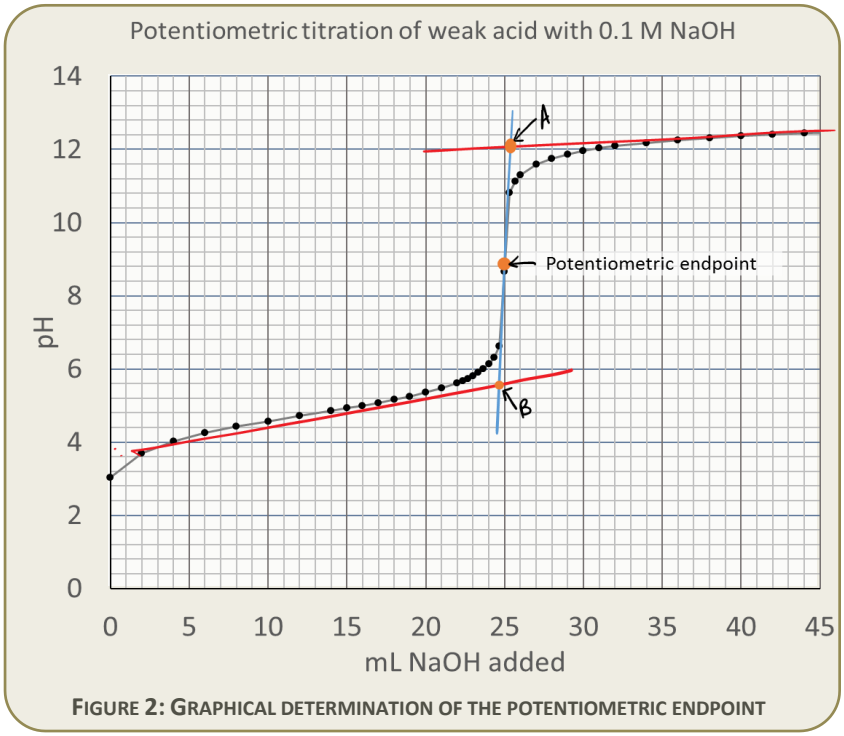

FIGURE 2: GRAPHICAL DETERMINATION OF THE POTENTIOMETRIC ENDPOINT

Your raw data tables should have columns for: *buret reading, volume delivered,* and *pH* as well as your unknown number and NaOH concentration. Expect ~40 data points for each titration.

Preparing for lab

Before coming to lab, make sure you have:

- Read Experiment 4 and Appendix I – print these and bring them with you to lab.
- Completed the online pre-lab quiz – *at least one hour before lab*
- Prepared raw data tables in your 'blue book' to use in lab
- Prepared yourself by wearing clothing that will completely cover you below the knee and a lab coat, with long hair tied back.

Experimental Procedure

For this experiment you will work in pairs.
Each partner must submit an individually written lab report.

Notes

1. In these experiments, you will measure low concentrations of hydrogen ions. Your apparatus must be *absolutely clean* if you are to obtain reasonable results. You should rinse all glassware two or three times with R.O. water before use. Your calibration beakers should also be rinsed with a small amount of the buffer solution before filling.

2. You must rinse the pH probe thoroughly with R.O. water each time you change solutions. During your measurements, you need to immerse the probe at least 2.5 cm below surface of the liquid. At the end of the lab period, you should rinse the pH probe and store it in **fresh R.O. water**.

Part 1: Potentiometric Titration of a Dilute Unknown Acid

Without these numbers, you cannot complete your report!

1. **Prepare your set-up:**
   - ↪ In your 'blue book', record the **unknown number** of the unknown acid solution assigned by your TA and the **exact concentration** of the NaOH solution you will use.
   - ↪ **Obtain** a 50 mL burette and a plastic beaker to use for the titration.
   - ↪ Calibrate the pH meter using ~30 mL each of the pH 4 and pH 9 buffers provided. Refer to **Appendix I** and your TA's pre-lab talk for detailed instructions on using the pH meter.
   - ↪ Fill a *clean* 50 mL burette with the ~0.15 M NaOH solution provided.

2. **Prepare your acid:** Dilute the unknown acid sample **by a factor of five,** using a 25.00 mL pipet and a 250.0 mL volumetric flask. This diluted acid will be used in the titration for Part 1.
   - During the experiment, keep your flask stoppered to minimize evaporation of the solvent and contamination of your solution.

Remember: adding water to your already-measured acid sample does not change the number of moles of acid in the beaker.

3. **Prepare your titration sample**:
   - ↪ Pipette a 25.00 mL aliquot of your diluted acid into the plastic beaker.
   - ↪ Add ~100 mL of R.O. water to make sure your solution is deep enough to cover the pH probe tip.
   - ↪ Add 5 drops of phenolphthalein indicator and a magnetic stir bar.

4. **Set up** your pH meter, pH probe, stir plate, burette, and beaker of solution as shown by your TA's demonstration apparatus. Ensure that:
   - Your pH probe is sufficiently immersed in the solution (>2.5 cm) to generate a stable measurement.
   - Your pH probe is not so close to the stir bar that they will touch.
   - The burette tip is below the rim of the beaker (to avoid splashing) without touching the acid solution.
   - The stirplate is set to a moderate speed – there should not be a vortex in your solution.

You will be adding ~30 mL of NaOH to the beaker – leave some room.

Stirring too fast may cause inaccurate pH readings, lose solution by splashing, or damage the pH probe.

5. **Titrate your diluted acid:**
   - ↪ Record the initial volume reading from the burette and the initial pH.
   - ↪ Add ~2 mL of NaOH from the burette. Record the new volume on the burette and solution pH. Repeat this (add ~2 mL of NaOH, record pH and volume) until the solution pH is close to 4.0.
   - ↪ Once your solution pH is **at or just above 4.0**, add the NaOH in 1 mL increments, recording the burette volume and solution pH after each addition.
   - ↪ When the solution pH is **at or just above 5.0**, add the NaOH 5 drops at a time. After each addition, record the burette volume and solution pH.
     - During this stage, you should notice the visual endpoint of the titration. Record in your data table the addition during which the color change occurred.
   - ↪ After the solution pH is **above 11.0**, you can resume adding NaOH in 2 mL increments, recording the burette volume and solution pH after each addition. Continue adding NaOH until you have added at least 47 mL to your beaker.

Take all burette readings to <u>two</u> decimal places.

Watch out - When cleaning up, don't drop your stir bar into the waste container!

Part 2: Titration of a More Dilute Unknown Acid

6. **Prepare your acid**: Using the diluted acid you prepared in Part 1, prepare a second dilution, using 50.00 mL of the dilute acid and a 100 mL volumetric flask. This diluted acid will be used in the titration for Part 2.

7. **Prepare your set-up:** Refill your buret with NaOH solution and rinse out your plastic beaker to use again in this titration.

8. **Prepare your titration sample**:
   - ↪ Pipette a 25.00 mL aliquot of the 10x diluted acid you prepared in Step 6 into the plastic beaker.
   - ↪ Add ~100 mL of R.O. water to make sure your solution is deep enough to cover the pH probe tip.
   - ↪ Add 5 drops of phenolphthalein indicator and a magnetic stir bar.

You will be adding ~30 mL of NaOH to the beaker – leave some room.

9. **Set up** your pH meter, pH probe, stir plate, burette, and beaker of solution as you did in Part 1. Ensure that:
   - Your pH probe is sufficiently immersed in the solution.
   - Your pH probe and stir bar don't touch, and the stir speed is moderate.
   - The burette tip is below the rim of the beaker without touching the acid solution.

Stirring too fast may cause inaccurate pH readings, lose solution by splashing, or damage the pH probe.

Take all burette readings to two decimal places.

10. **Titrate your diluted acid:**
    - ↪ Record the initial volume reading from the burette and the initial pH.
    - ↪ Add ~1 mL of NaOH from the burette. Record the new volume on the burette and solution pH. Repeat this (add ~1 mL of NaOH, record pH and volume) until the solution pH is close to 4.0.
    - ↪ Once your solution pH is **at or just above 4.0**, add the NaOH in 0.5 mL increments, recording the burette volume and solution pH after each addition.
    - ↪ When the solution pH is **at or just above 5.0**, add the NaOH 3 drops at a time. After each addition, record the burette volume and solution pH.
      - During this stage, you should notice the visual endpoint of the titration. Record in your data table the addition during which the color change occurred.

Watch out - When cleaning up, don't drop your stir bar into the waste container!

11. After the solution pH is **above 11.0**, you can resume adding NaOH in 1 mL increments, recording the burette volume and solution pH after each addition. Continue adding NaOH until you have added at least 23 mL to your beaker, or you have 5 measurements above 11.0, whichever is the larger volume.

Sitting too long in the high-pH solution will damage the pH probe.

12. When you are finished, in addition to cleaning your glassware and work area, rinse your pH probe and store it in a bottle of **fresh** R.O. water.

Calculations (done outside lab)

1. Plot a titration curve for each titration of your unknown acid **(see instructions below)**, following the example in the Introduction to this experiment.
2. Use your titration curve to identify the potentiometric endpoint, visual endpoint, and half-equivalence point.
3. Based on your observed endpoints, determine *for each titration*:
    a. The concentration of your diluted acid sample (25.00 mL aliquot).
    b. The concentration of the original unknown acid sample (as given to you by your TA).

If your experimental value is ambiguous, list the two closest acids and justify the reason why you cannot choose one over the other.

4. Use your titration curves and the list of available unknown acids at the end of this Experiment to identify your unknown acid.

    Be sure to explain how you dealt with any differences between your two titrations in either concentration or identity of the unknown acid.

Making your Titration Curves

You will be interpolating and reading points from your titration curve in order to determine the endpoint and half equivalence point for each titration – use these guidelines to make sure you make a graph that can be read accurately:

Remember – readings from your graph can only be as precise as your gridlines!

- Make your graph **large** – it should take up as much of one letter-size page as possible.
- Have **dense gridlines** – if you are plotting by hand, use metric graph paper with 1-mm gridlines. If you are plotting on a computer, set your 'minor' gridlines to

be *at least* every 0.2 – 0.5 mL (x-axis) and every 0.2 – 0.5 pH units (y axis). Make your plot large enough that it will be readable when printed.

- **Hand-draw** your curve of best fit, whether or not you plot your data points on the computer.

Hand-drawing allows you to exclude any outliers and draw a **smooth** "S-curve" shape through your data.

On your plot, you should also include the following parts, **hand-drawn and labelled clearly**:

- The "lines of best fit" used to determine the potentiometric endpoint
- The locations of potentiometric **and** visual endpoints – mark these on the curve and note the pH and V_{NaOH} for each.
- The half-equivalence point – marked on the curve and labelled with the pH and V_{NaOH}.

Refer to the Introduction section of Experiment 4 for details on locating these points.

Lab Report

You will have **one week** to complete your formal lab report. Your report must be handwritten in ink in a blue lab notebook (with the exception of graphs, which may be hand-drawn in pencil or plotted by computer and stapled into the book).

Refer to the lab manual Introduction chapter for details on formal reports.

Submit your completed report to your lab section's dropbox outside SA 116. If your report Is late, hand it in to the *Late Report Box* outside SA116, and notify your TA and the Lab Coordinator when you have submitted it. Marks will be deducted for late reports: 1 mark per half-day and 1 mark per weekend day.

Marks Breakdown

The general marking scheme for the lab report is as follows:

Criteria	Marks
Introduction Objective is clear, techniques and analyses are described	2
Procedure Statement of procedure, including additions or changes.	1
Data Data tables present and formatted appropriately	1
Data: Plots Graph has correct formatting, displays relevant information, and values are clearly labelled	2
Data: Results & Calculations Unknown acid is identified correctly (including concentration). Sample calculations for each step are included and correct.	3
Discussion Major results are re-stated and placed in context of the techniques used. Techniques used are evaluated and compared.	2
Discussion: Accuracy & Precision Accuracy and reproducibility of results is evaluated, with numeric support (for pKa and acid concentration)	2
Discussion: Sources of Error At least two appropriate sources of error are discussed in the context of the results. (at least one non-"human error")	1
Conclusion & References Objectives, results, and their reliability are summarized. Reference list is consistently formatted, includes all required sources, and makes use of in-text citations.	2

TABLE 4.1: K_A VALUES FOR AQUEOUS SOLUTIONS AT 298 K, WHERE K_w = 1.01 x 10^{-14}

Acid	K_a
Acetic (CH_3COOH)	1.75×10^{-5}
Monochloroacetic ($CH_2ClCOOH$)	1.50×10^{-3}
Dichloroacetic ($CHCl_2COOH$)	5.00×10^{-2}
Trichloroacetic (CCl_3COOH)	1.30×10^{-1}
Benzoic (C_6H_5COOH)	6.30×10^{-5}
Boric ($B(OH)_3$)	5.88×10^{-10}
Carbonic (H_2CO_3) HCO_3^-	4.77×10^{-7} 4.68×10^{-11}
Formic ($HCOOH$)	1.78×10^{-4}
Hydrofluoric (HF)	6.80×10^{-4}
Hydrosulphuric (H_2S) HS^-	1.00×10^{-7} 1.00×10^{-15}
Hypochlorous ($HOCl$)	2.80×10^{-8}
Nitrous (HNO_2)	5.10×10^{-4}
Oxalic $(COOH)_2$ $HOOCCOO^-$	5.60×10^{-2} 5.30×10^{-5}
Phenol (C_6H_5OH)	1.10×10^{-10}
Phosphoric (H_3PO_4) $H_2PO_4^-$ HPO_4^{2-}	7.50×10^{-3} 6.16×10^{-8} 4.80×10^{-13}
Phthalic $C_6H_4(COOH)_2$ $C_6H_4(COOH)COO^-$	1.20×10^{-3} 3.90×10^{-6}
Propanoic (C_2H_5COOH)	1.30×10^{-5}
Sulfuric (H_2SO_4) is a strong acid, but only the first deprotonation. HSO_4^-	1.00×10^{-2}
Sulfurous (H_2SO_3) HSO_3^-	1.70×10^{-2} 6.30×10^{-8}

Procedure Flow Chart: Pre-Lab Assignment

Complete the experimental flowchart with details from each step of the procedure.

TA Initials:

Before beginning:

Part 1

1b. Calibrate pH meter

Preparation:
2 50 mL beakers
Rinse with RO then buffer
one each: pH 4 and pH 9
Get pH meter and probe,
power on.

Calibrate:
-Meter should say "A" (press READ)
-Hold CAL till √ appears
-Put probe into buffer
-When pH stable, push CAL
-Repeat with other buffer

Cleanup: