

Experiment 4

Identification of unknown acids by titration

In this experiment, you will use titration to determine the identity and concentration of two unknown weak monoprotic acids. You will compare visual and potentiometric titration methods, and you will demonstrate the effects of concentration and the acid ionization constant (K_a) on titration curves.

What laboratory techniques and skills will you learn?

- Volumetric techniques, e.g. Serial dilution and solution preparation
- Performing acid-base titrations
- Determining the identity of an unknown acid
- Calibrating and using a pH meter

What chemical concepts will you apply?

- Solution concentration and dilutions *Open Stax Section 3.3*
- pH of solutions of weak acids/bases *Open Stax 14.3*
Open Stax 14.2 (significant figures)
- Acid-Base Titrations *Open Stax 4.5 - Titrations*
Open Stax 14.7

What communication and reporting skills will you use?

- Preparing data collection tables
- Presenting and interpreting data from graphs
- Using a potentiometric titration curve to determine the endpoint of a titration
- Writing a complete formal lab report

Pre-lab preparation

- ☐ Read the procedure & highlight **margin questions** to discuss with your TA
- ☐ Complete the **pre-lab quiz** on D2L

What to bring to lab

- ☐ Experiment 4 Procedure
- ☐ Data set assigned to you
- ☐ Appendices **B, D, F** and **H**

Assessment

You will hand in this laboratory report TWO weeks after your lab. Additional report guidelines regarding submission will be posted to D2L.

Don't forget to use the How-to Write Formal Reports guide, and feedback from Experiment 2 and 3 to help you meet the requirements listed for this full formal report.

Background

In this experiment, you will use both qualitative and quantitative properties to determine an unknown acid's identity 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 comparing your data to a titration of a different unknown acid, you will also be able to compare the changes in the titration curve due to the equilibrium acid ionization constant (K_a), and compare the effectiveness of the two titration methods.

What is a titration?

Titration is a method used to determine the concentration of one solution by reacting it with a second solution that we know the concentration of very precisely.

A typical set-up for a titration is shown in **Figure 1**. Usually, the buret is filled with titrant (the solution of known concentration – yellow in the diagram), while some of the analyte (the solution we are trying to analyze) is placed in a flask. The titrant is slowly added, until exactly enough titrant has been added to react with all of the analyte in the flask – this is the equivalence point.

Usually, we cannot see the equivalence point directly. To help make the endpoint visible, we can use a color indicator – a compound that will be one color before the equivalence point, and a different color after. One color indicator you may be familiar with is phenolphthalein, which is clear in acidic solution, changing to bright pink in basic solutions. Since the color change of the indicator may not happen exactly at the equivalence point, the point where the indicator changes color (and we usually stop titrating) is called the **endpoint**. The volume of titrant needed to reach this point is the titre.

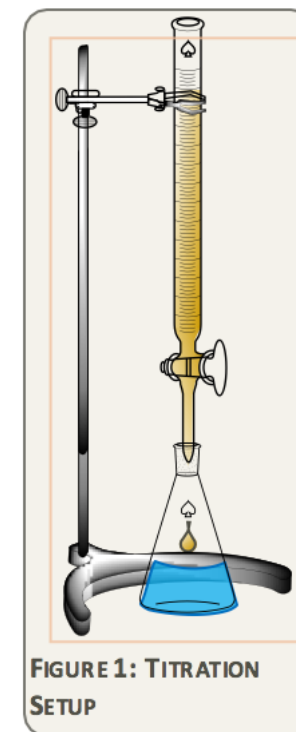
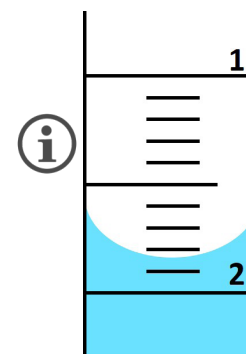


FIGURE 1: TITRATION SETUP



We read the burette from the bottom of the meniscus, to a precision of 2 decimal places, e.g. 1.85 mL.

More information on taking precise buret readings can be found on Page A13 (Appendix D).

For any titration, knowing the relationship between the moles of analyte in your titration sample and the **moles of titrant used to reach the equivalence point** will allow you to determine the concentration of your analyte. With care, manual titrations can be extremely accurate – although many modern laboratories carry out analyses instrumentally, manual titrations are still commonly performed.

Acid-base Titrations

In this experiment, we are performing an acid-base titration, where the reaction involved is a neutralization reaction.

Neutralization of a weak acid “HA”: $\text{HA (aq)} + \text{OH}^- \text{ (aq)} \rightarrow \text{A}^- \text{ (aq)} + \text{H}_2\text{O (l)}$ [1]

Neutralization is an ideal 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. 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

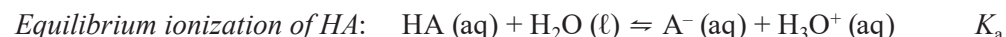
In a potentiometric titration, we will plot the pH of the analyte against the amount of titrant added. By using a pH probe to monitor the acidity of the solution, we can determine the endpoint without relying on a color indicator. A typical plot of pH vs. mL of titrant added for the titration of a weak acid is shown in **Figure 2**, 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.



Related equilibria and K:

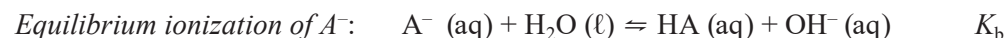
What is the reverse of reaction [1]? If A^- is a weak base, what do we know about K_{eq} for the reverse reaction? Based on this, why can we safely assume that reaction 1 has a very large K (and therefore goes to completion)?

- A. Initial pH:** Before any titrant is added, the major species in solution is the **weak acid**; therefore, the pH is determined only by the equilibrium ionization the weak acid as it reacts with water to produce the conjugate base.

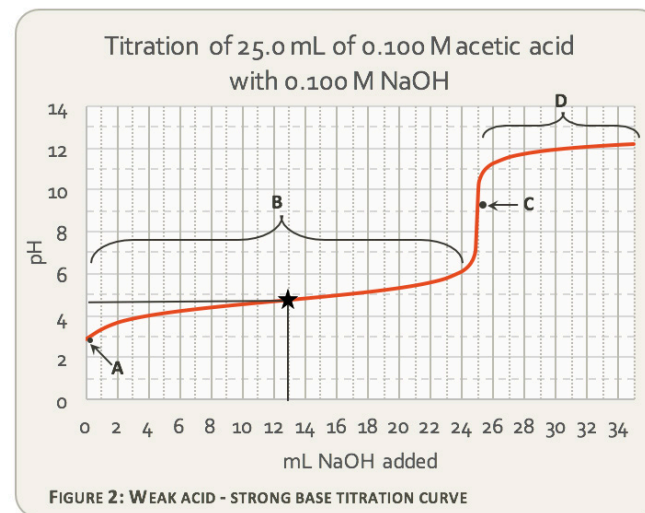


- B. Buffer region:** Once some titrant is added, there will be significant amounts of *both* the **weak acid** and its **conjugate base** present in the flask. This creates a buffer – notice that the pH changes slowly as titrant is added in this region. The point on the titration curve marked with a star (★) is the half-equivalence point – the point when enough base has been added to react with exactly half of the weak acid present.

- C. Equivalence point:** At this point, exactly enough strong base has been added to react with all of the weak acid in solution, leaving the **conjugate base** as the only major species in solution. 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.*



- 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.



Finding the Equivalence Point and Endpoint

As stated before, we need to figure out the **amount of titrant required to reach the equivalence point** in order to determine the concentration of our analyte. To do this, we rely on having some *observable* cue that we've reached this point in the titration, and we assume that this observed **endpoint** occurs as near as possible to the **equivalence** point.

Visual titrations (with color indicators)

In visual titrations, the first persistent color change is taken as the endpoint. What color change this 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 using the first derivative approximation method. This process is described in detail in the report guidelines at the end of this document.

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



To safely assume that the **endpoint** is an accurate representation of the **equivalence** point...

- for a **visual** titration, the colour indicator must change colour as close as possible to the pH at equivalence, or
- for a **potentiometric** titration, there must be sufficient data points to allow the endpoint to be correctly read from the titration curve.

Identifying a weak acid

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:

$$\text{mol OH}^- \text{ added} = \frac{1}{2} \text{ mol "HA" in flask}$$

The OH^- added will react 1:1 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 2** as an example:

Amount of acetic acid: $25.0 \text{ mL} \times 0.100 \text{ M} = 2.50 \text{ mmol}$ acetic acid
Amount of OH^- to reach $\frac{1}{2}$ -equivalence point: $2.50 \text{ mmol} \div 2 = 1.25 \text{ mmol}$ OH^- needed
that is... $1.25 \text{ mmol OH}^- \div 0.100 \text{ M} = 12.5 \text{ mL OH}^-$ solution needed

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

	HA	+	OH^-	$\rightarrow$	A^-	+	H_2O
Initial (mmol)	2.50		1.25		0		---
Change (mmol)	-1.25		-1.25		+1.25		---
Final (mmol)	1.25		0		1.25		---
Final (M)	0.0333		0		0.0333		

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-Hasselbalch relation to predict the pH of this mixture:

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

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

$$pH = pK_a$$



Notice that the new concentrations of HA and A^- are not half of the original concentration, since we are also changing the total volume of the solution during the titration.



Check this calculation: At half-equivalence, what is the total volume of the solution in this case? Does the concentration given here agree with your value?



The **Henderson-Hasselbalch equation** can only be used in the buffer region of a titration (region B in Figure 2), where the concentrations of the conjugate acid and conjugate base in solution are relatively similar (within 100x). *See section 14.6 in your Open Stax textbook for more information.*

In other words, no matter what the original concentrations were, at the half-equivalence point, $\text{pH} = \text{pK}_a$. 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 2**, 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.

Use the questions at the left to see how you will reverse this process in the lab.

Procedure

The following procedure will be demonstrated in **Videos E4-A** and **E4-B** available on D2L. Be sure to record your observations.

- **Videos E4-A-i** focuses on a sample preparation
- **Videos E4-A-ii** focuses on the visual titration of an unknown acid
- **Videos E4-B-i** focuses on the calibration of a pH meter
- **Videos E4-B-ii** focuses on the potentiometric titration of an unknown acid

You will be assigned a dataset that contains data to generate 2 titration curves: one graph will be prepared during the “in-lab guided data analysis activity” with the help of your TA and one will need to be completed after the lab time, as part of your lab report.

Part A. *Visual Titration of a Dilute Unknown Acid*

Throughout this lab, always pipet from a transfer beaker, never directly from a volumetric flask or bottle.

1. **Prepare your diluted acid:** Collect 35 mL of your assigned unknown acid in a 50 mL beaker. Prepare a diluted solution of your unknown acid by pipetting 25.00 mL into a 250.00 mL volumetric flask and diluting with R.O. water.



How does this calculation differ from your lab?

The calculation on the previous page uses a known *concentration* and *volume* of a *known* weak acid.

For your sample in the lab, which of these parameters will you know at the start of your experiment?

What will finding the endpoint (or equivalence point) allow you to determine?

How can you determine the location of the half-equivalence point from your endpoint?



During the experiment, keep your flask stoppered to minimize evaporation of the solvent and contamination of your solution.

2. Prepare your visual titration sample:

- Pipette a 25.00 mL aliquot of your diluted acid into a 250 mL plastic cup. Label and set aside this pipet for later use.
- Add ~100 mL of R.O. water
- Add 5 drops of phenolphthalein indicator and a magnetic stir bar.

3. Set up for a visual titration. Fill your clean 50 mL burette between the 0-1 mL marks with the ~0.15 M NaOH solution provided. Ensure that:

- The burette tip is below the rim of the plastic cup (to avoid splashing) without touching the acid solution.
- The stirplate is at a moderate speed – there should be no vortex in your solution.



Sodium hydroxide (NaOH) is corrosive and should be handled with care. To ensure your safety, when filling your burette, make sure to...

- lower the burette so that the top is **at or below eye-level** before pouring any solution
- **use your long-stem funnel** to avoid spillage when pouring

6. Titrate your diluted acid visually to determine an approximate endpoint:

- a. Record the **initial volume reading** from the burette.
- b. Add NaOH from the burette in ~2 mL increments until you begin to see a *faint pink colour in your solution*.
- c. Continue adding NaOH in smaller (~1 mL) increments until a *persistent pale pink* colour appears in the solution. This point is your **approximate visual endpoint**. Record the **volume of NaOH solution** added to reach this point (V_{est}).



Before you begin Part B, use your V_{est} value to fill in the increments (volumes of NaOH) in the **table at the bottom of Page 10**. This will be your guide to performing a precise potentiometric titration for your dilute acid. Your TA must check your completed table **before** you proceed.

Part B. Potentiometric Titration of a Dilute Unknown Acid**Solution preparation****7. Prepare your potentiometric titration sample:**

- Rinse the plastic cup and stirbar with RO water to prepare for a new titration.
- Pipette a new 25.00 mL aliquot of your diluted acid into your plastic cup. *Set aside the remaining solution until your TA has initialed your completed potentiometric titration data, in case you need to repeat your titration.*



Be careful when cleaning and rinsing- don't let your stirbar fall into the waste container!



Always keep your pH probe immersed in a solution. When not in use, immerse the probe in a beaker with RO water.

- Add ~100 mL of R.O. water.
- Add 5 drops of phenolphthalein indicator and the magnetic stir bar.

8. **Refill your burette** with the ~0.15 M NaOH solution to ensure there is at least 40 mL of NaOH available for titration.

pH meter calibration and setup

9. **Calibrate the pH meter** with both the pH 4 and pH 9 buffers provided. For each buffer solution, collect ~30 mL of solution in a 50 mL beaker that you have rinsed with a small amount of that buffer solution. Refer to **Appendix H** for detailed instructions on using the pH meter. *Label and set aside both beakers of buffer solution after calibration, in case you need to re-calibrate during the lab period.*

10. **Set up your titration apparatus as in Step 3, but add the pH meter and probe.** In addition to the guidelines in Step 3, also ensure that:

- Your pH probe is sufficiently immersed in the solution to generate a stable measurement (*at least 2.5 cm below surface of the liquid*).
- Your pH probe is not so close to the stir bar that they will touch.
- Your pH meter is set for measurements in Continuous or “live” mode (see **Appendix H**).

11. **Titrate your diluted acid potentiometrically, collecting pH and volume information in your prepared table:**

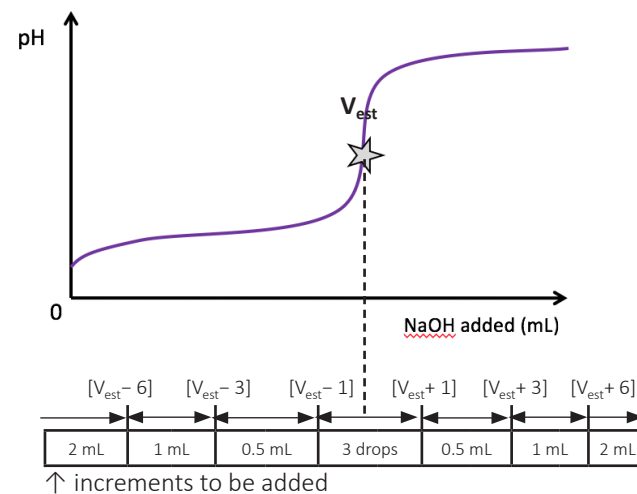
- Record the initial volume reading from the burette and the initial pH.
- Add ~2 mL of NaOH from the burette. Record the new volume on the burette and solution pH.
- Repeat this (add ~2 mL of NaOH, record pH and volume) until the solution pH is **6 mL away from your approximate visual endpoint volume (V_{est})**.



Varying precision: We have been very precise with our measurements up to this point, using volumetric pipets and volumetric flasks. Why do we **not** need to precisely measure the volume of water added here?



To perform our titration with sufficient precision, we need to ensure that we add smaller and smaller increments as we approach the equivalence point, since the pH changes steeply near this point. You will use your approximate visual endpoint to determine when to reduce the volume of NaOH added in each increment.



e.g. if your visual endpoint in Part 1 was $V_{\text{est}} = 15.50$ mL, then, during your titration you must add NaOH in 2 mL increments until you reach 9.50 mL. At that point, start adding NaOH in 1 mL increments until 12.50 mL, *etc.*

- d. Continue adding NaOH in 1.0 mL increments, recording the burette volume and solution pH after each addition, until you are **3 mL away from V_{est}** .
- e. Switch to adding NaOH in ~0.5 mL increments, recording the burette volume and solution pH after each addition, until you are **1 mL away from V_{est}** . After each addition, record the burette volume and solution pH.
- f. Now add NaOH in 3 drop increments. After each addition, record the burette volume and solution pH.
- g. During this stage, you should notice the *more precise* **visual endpoint of the titration**. Record in your data table the addition during which the color change occurred (V_{visual}).
- h. Continue adding in the increments described in your table, recording the burette volume and solution pH after each addition, until you have added at least 30 mL to your plastic cup.



Do not begin to increase the size of your volume increments until you have **actually** seen your visual endpoint, regardless of what you had originally planned in your table on Page 10.

Part C. Reference data collection & clean up

10. Before leaving the lab, rinse your pH probe and use it to **measure the pH of a fresh sample of RO water** for reference.
11. 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** (*i.e.* empty out the R.O. water in the storage bottle and refill the bottle with fresh R.O. water before placing your pH probe inside).



Before you measure: What pH do you expect to measure for a sample of pure water at room temperature?

After you measure: Is the pH you measured equal to the pH you predicted? *Given the ways that you have used RO water throughout your experiment, how do you expect your results might be affected?*

In-Lab Guided Data Analysis Activity

Before you leave the lab meeting, your TA will help you practice how to generate a titration curve and how to analyze it to identify an unknown acid and determine its concentration. You will need to include a copy of this graph in your lab report.

Take good notes as you complete these tasks, so that you can refer to these as a resource to help you when you approach your own data outside of the lab.

Laboratory Report Guidelines for Experiment 4

Complete the Word document “**Experiment 4 Report**” provided on D2L using the specific data set provided to you. You will need to insert copies of your titration graphs generated using Excel into your word document.

Submit your electronic report as a **PDF on D2L (dropbox folder)**, before the start of your **next tutorial** (Tutorial 5). Marks will be deducted for late reports.



BEFORE you begin writing...

Read the guide ‘**How to write CHEM 203 formal reports**’

Results section – *Plotting your Titration Curves*

Plot a titration curve from the potentiometric titration data collected for **each** of the two dilute unknown acids (*one of them being from the in-lab analysis activity*). You will use these graphs to determine the endpoint and half-equivalence point for each titration – use these specific guidelines to make sure you make a graph that can be read accurately

- ☐ **Make each graph large** – it should take up as much of one letter-size page as possible.
- ☐ Don't forget to include a descriptive title, include unknown number.
- ☐ Make sure you include lots of gridlines to help you read values from the graphs.

Results section – Finding a Potentiometric Endpoint

To determine the potentiometric endpoint as accurately as possible, we will use a “*first derivative method*”. The equivalence point in a titration curve corresponds technically to the point where the titration curve is the steepest. This would correspond to the point where the first derivative (slope) would be maximum. You can see an example of that on the right hand side. When the volume is 15.55 mL, the first derivative reaches a maximum. Hence, for this dataset, the potentiometric endpoint to be used in the concentration calculations would be 15.55 mL.

To help you prepare this first derivative graph and find your potentiometric endpoint, we have prepared an excel template and incorporated it on one sheet of your Excel dataset for Experiment 4.

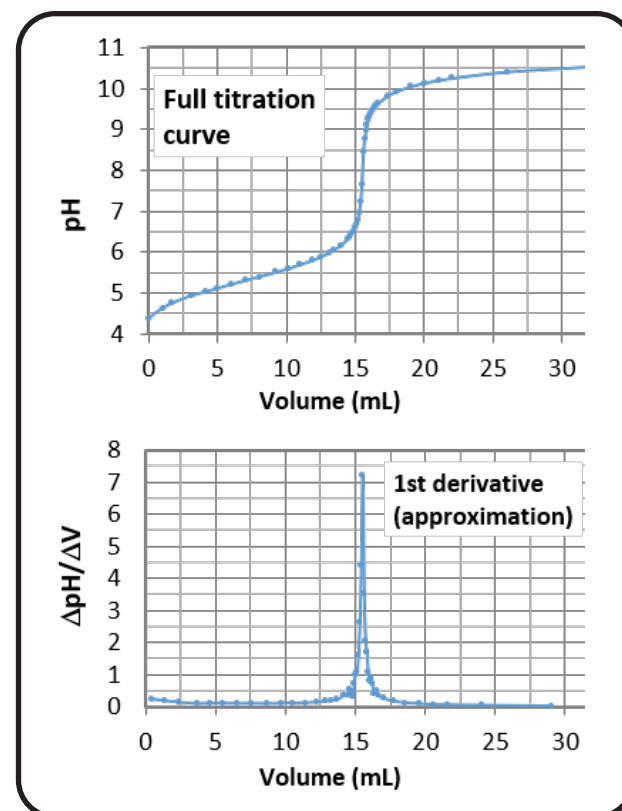
Results section – Labelling your Titration Curves

On each graph, you should include the following items, **labelled clearly**:

- The locations of **potentiometric** and **visual endpoints** – mark these on the curve and note the coordinates (V_{NaOH} , pH) for each.
- The **half-equivalence point** – marked on the curve and labelled with its coordinates, in the form (V_{NaOH} , pH)

Results section – Summary Tables

After you complete your graphs, **summarize** key values obtained from both titration curves in a single table, to make comparing between these two titrations easier:



		Unknown # _____	Unknown - in lab analysis
Volume NaOH added	At the visual endpoint		
	At the potentiometric endpoint		
	At ½-equivalence		
pH	At ½-equivalence		

Prepare a *second* table to **summarize** all *calculated* values for your two unknowns:

	Unknown # _____	Unknown - in lab analysis
Dilute acid concentration		
Original (stock) acid concentration		
Acid ionization constant, K_a		
% Error in K_a		
Acid identity		

Results section – Sample Calculations for one unknown acid

Include sample calculations for all of the values calculated in your second summary table. When determining your concentrations, note that the **dilute acid** refers to the concentration at the end of procedure Step 4, of which you have used 25.00 mL for each titration. The original (stock) acid refers to the concentration in bottles on the benchtop.

Make sure to show how you calculated K_a from your data and use the list of available unknown acids in **Table 4.1** in this Experiment to identify your acid.

Discussion section – Hints

When asked to state your key findings & put your results in context ...

Remember that you should report the findings needed to address each of your objectives.

As just one hint, this means that *one* of the questions your discussion should answer is, “How do acid concentration and K_a affect titration curves?” To answer this question in the context of your data, focus *just* on comparing the values **in your two summary tables**:

Were the *concentrations* **similar or different**? Were the *ionization constants* **similar or different**? Can you **connect** this to what’s similar or different in your other summary table?

Based on your observations, draw some conclusions about how your **½-equivalence pH** and V_{NaOH} would change if... (i) the concentration of acid was increased, or, (ii) the acid had a larger K_a , or (iii) the NaOH concentration used as the titrant was increased.

When asked to comment on accuracy and precision...

Compare the **relative accuracy of your two potentiometric datasets (one for each acid)**, with reference to the % error values you calculated. Given the list of acids in Table 4.1, *how certain are you of the identity of your unknown acids? Explain.* Comment on the relative precision or reproducibility of your **visual vs. potentiometric titrations**.

When asked to comment on experimental limitations...

Make sure that you address potential limitations or sources of uncertainty for each type of titration, in addition to sources of error in the experiment as a whole.

Introduction section – Hints

When writing about ‘**Why did we do this experiment?**’ don’t forget that...

- ... there are several objectives for this experiment.
- ... there are multiple chemical reactions occurring- which one accomplishes key objectives?

When writing about ‘**Why did we do this experiment this way?**’, don’t forget to...

- ... explain *what a titration is* in order to justify *why titration is used here*.
- ... highlight features and differences between the *two types of titration* performed
- ... define *key points on the titration curve* used to accomplish the objectives, in terms of the relative amounts of species in solution.

TABLE 4.1: K_a VALUES FOR AQUEOUS SOLUTIONS
AT 298 K, WHERE $K_w = 1.00 \times 10^{-14}$

Acid	Ionization constant (K_a)
Monochloroacetic (CH_2ClCOOH)	1.50×10^{-3}
Dichloroacetic (CHCl_2COOH)	5.00×10^{-2}
Trichloroacetic (CCl_3COOH)	1.30×10^{-1}
Carbonic (H_2CO_3)	4.77×10^{-7}
Bicarbonate (HCO_3^-)	4.68×10^{-11}
Formic (HCOOH)	1.78×10^{-4}
Hypochlorous (HOCl)	2.80×10^{-8}
Phenol ($\text{C}_6\text{H}_5\text{OH}$)	1.10×10^{-10}
Propanoic ($\text{C}_2\text{H}_5\text{COOH}$)	1.30×10^{-5}
Hydrogen phthalate ($\text{C}_6\text{H}_4(\text{COOH})\text{COO}^-$)	3.90×10^{-6}
Acetic Acid (CH_3COOH)	1.76×10^{-5}

Procedure section – *Hints*

Don't forget to include a short procedure section. Refer to Experiment 3 for an example.

Conclusion section – *Hints*

Don't forget to include a short conclusion section. Refer to Experiments 2 & 3.

Reference section – *Hints*

Don't forget to include a short reference section. Refer to Experiments 2 & 3.



BEFORE YOU SUBMIT, check:

- Have you carefully followed all the detailed **formatting guidelines** in the How-to Write Formal Reports?
- Have you included your **data tables and graphs** in your report?