Characterization of an Unknown Acid

Goal and Overview

The probable identity of an unknown solid weak acid will be determined. Interpretation of titration curve data will allow the molar mass and pK_a of the acid to be found, and the approximate melting point of the acid will be investigated using a Meltemp apparatus.

Objectives and Science Skills

Perform titrations of an unknown acid solution while recording pH as a function of added base.
Plot experimental titration data and interpret the graphs to determine the approximate pK_a and moles of acid in solution.
Use a Meltemp apparatus to determine the approximate melting point of the solid acid.
Evaluate the results for molar mass, pK_a, and melting point to determine the probable identify of the unknown acid from a list of choices.
Quantitatively and qualitatively compare experimental results with theoretical values.
Identify and discuss factors or effects that may contribute to deviations between theoretical and experimental results and formulate optimization strategies.

Suggested Review and External Reading

Reference materials and textbook sections on equilibrium, titration, weak acids and bases, and phase changes

Introduction

A weak acid, HA, does not dissociate completely in water. The extent of dissociation and position of equilibrium are quantified by the acid dissociation constant, K_a. The weak acids considered in this experiment have K_a values between $\sim 10^{-2}$ to $\sim 10^{-7}$.

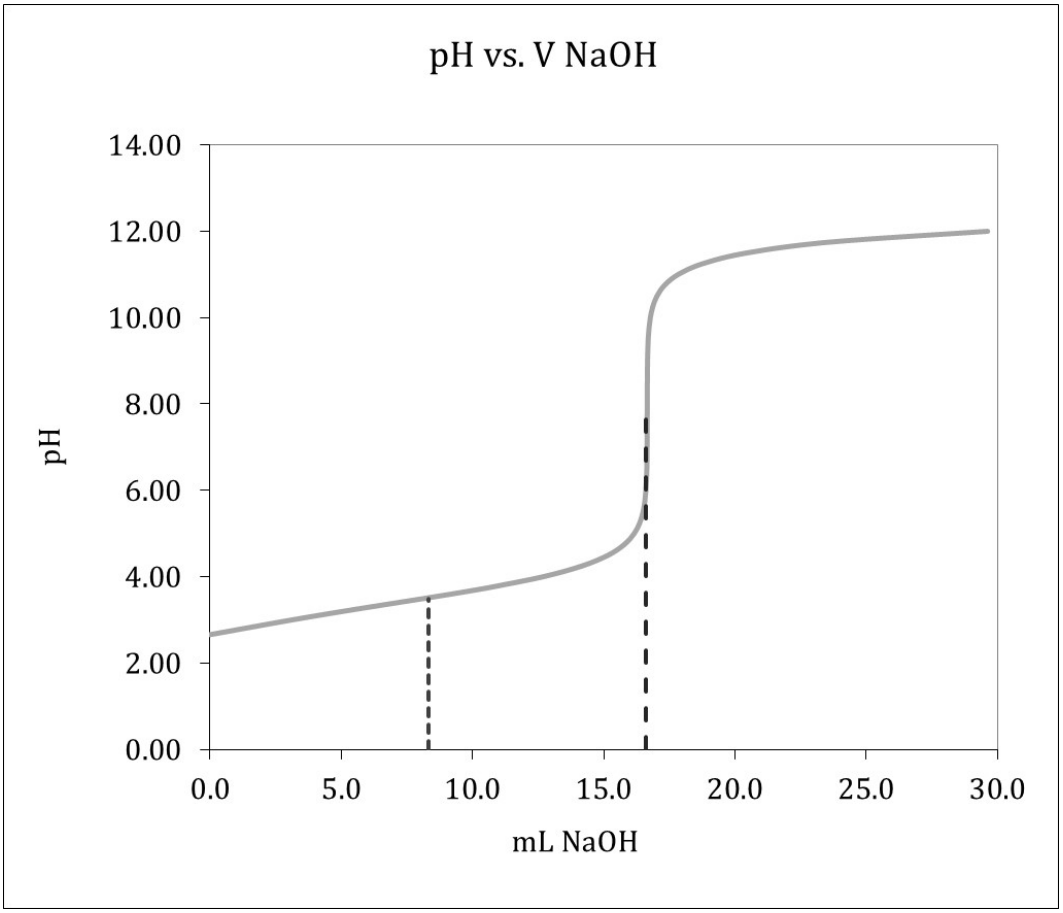
$$HA \rightleftharpoons H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

To simplify equations, reactions and equilibria will be written in terms of H^+ (instead of H_3O^+) and are assumed to occur in aqueous solution at 25°.

When an analyte solution containing a weak acid is titrated with a strong base titrant such as NaOH(aq), both $[H^+]$ and [HA] decrease while $[A^-]$ and pH increase as neutralization proceeds.

$HA + OH^- \rightarrow A^- + H_2O$

How the pH of the analyte solution changes during the course of a titration can be represented graphically on a titration curve, where pH is plotted vs. the volume of OH^- added. Two key points on the curve occur at the equivalence point and at halfway to the equivalence point. Although these points can be calculated precisely using first and second derivatives, it is typically sufficient to estimate them from the titration curve.



Equivalence point ($V_{OH^- \text{ added}} = V_{eq}$): The stoichiometric amount of OH^- has been added. The HA in the analyte has been exactly neutralized.

$$n_{OH^- \text{ added}} = n_{HA \text{ original}} = \left(V_{eq}\ in\ L\right) \times \left(M_{OH^-}\ in\ \frac{mol}{L}\right)$$

If the mass of HA in the analyte is known, the molar mass of HA can be calculated.

$$\mathrm{MM_{HA}} = \frac{\#\ \mathrm{g\ HA}}{\mathrm{mol\ HA}} = \frac{\mathrm{m_{HA\ in\ analyte}}\ in\ g\ from\ a\ balance\ measurement}{\mathrm{n_{HA\ total}}\ in\ mol\ from\ the\ titration\ curve\ analysis}$$

Half-equivalence point ($\mathrm{V_{OH^-\ added}} = {}^1\!/_2\,\mathrm{V_{eq}}$): Half of the stoichiometric amount of $\mathrm{OH^-}$ has been added. Half of the HA that was originally in the analyte has been neutralized and is present as $\mathrm{A^-}$.

$${}^1\!/_2\,\mathrm{HA_{original}} \xrightarrow{not\ neutralized} \mathrm{HA} \quad \text{and} \quad {}^1\!/_2\,\mathrm{HA_{original}} \xrightarrow{neutralized} \mathrm{A^-}$$

$$\mathrm{n_{HA}} = \mathrm{n_{A^-}} \xrightarrow{at\ equilibrium} [\mathrm{HA}] \approx [\mathrm{A^-}]$$

Assuming $[\mathrm{HA}] \approx [\mathrm{A^-}]$, the pH is approximately equal to the pK_a of HA.

$$K_a = [\mathrm{H^+}]\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} \approx [\mathrm{H^+}] \xrightarrow{-log} \mathrm{p}K_a \approx \mathrm{pH}$$

Melting point, T_m, is another distinguishing characteristic of the solid acid, but in lab it is typical to observe that the solid melts over a small temperature range. There can be a variety of reasons for this, including those related to the precision of the apparatus used. Although melting point data is somewhat unreliable, it provides further information regarding the solid acid's identity.

Equipment List

Analytical balance, weigh boats
Buret, buret clamp, ring stand
pH meter, stir plate, magnetic stir bar
Meltemp apparatus, thermometer, capillary tube
Miscellaneous labeled glassware, labeled deionized water wash bottle

Procedure

It is very important to watch your time. You need data for two good titrations and two melting points. You and your partner need to work together cooperatively and efficiently but you must also perform certain activities separately.

Please pay attention to your TA's demonstration and instructions. Please ask questions.

Person #1 in your pair should prepare the acid solution for a titration while person #2 performs a melting point measurement. Work together as a team for the titration, with person #1 controlling the buret and reading NaOH volumes while person #2 runs the pH

meter. Swap roles for the second trials. Make sure to have complete data for both titrations and melting point trials before leaving lab.

Obtain a vial of solid acid and record its number. This amount of acid should be sufficient for at least two titrations and two melting point determinations.

Caution

Solid organic acids can be mild skin irritants. Handle them carefully and wash your hands thoroughly.

Part 1. Titration of the unknown acid in solution

1. Using the analytical balance, mass out 0.3000 g of the acid. Record the mass to four decimal places. Please keep the balance clean.

2. Put the solid acid into a labeled 250-mL beaker.

3. Unless otherwise instructed, assume that the acid must be dissolved in a small volume of ethanol **before** water can be added. Take ~20 mL ethanol in a labeled graduated cylinder and add it to the beaker containing the solid acid. Gently swirl until the solid acid dissolved. Do **not** heat the solution.

4. Add ~80 mL deionized water to the acid-ethanol mixture. You **must** add the ethanol to dissolve the solid acid **before** adding water.

5. Carefully take about 50 mL NaOH in a small labeled beaker. This is enough to fill your buret one time. Record the molarity of the NaOH to four decimal places.

Once you see how much NaOH a single titration requires, you can take more if you need it. Please minimize the amount you waste (you cannot pour excess back into the reagent bottle).

6. Carefully fill your buret (see Caution below).

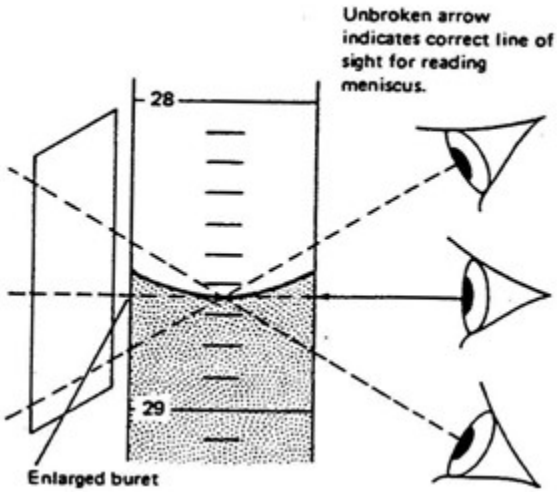
Record the initial volume reading, V_{in}, at the bottom of the meniscus to 2 decimal places. V_{in} does NOT need to be 0.00 mL.

Caution

Make sure that the buret is secure and straight in the buret clamp that is fastened to the stand. There should always be a labeled container under the buret large enough to capture the liquid contents.
Do not pour chemicals above eye level. You can carefully set the stand on the floor long enough to fill the buret. Use a funnel; have a labeled waste beaker beneath the buret; and, make sure that the stopcock is closed.
Carefully set the buret stand back on your lab bench. Allow a small amount of NaOH to pass through the tip into the waste beaker.

7. Record the initial volume, V_{in}, to two decimal places.

All volume readings from the buret should have two decimal places (__._0 or __._5 mL, for on a line or halfway between a line).



V = 28.65 mL; readings are usually ±0.05 mL

(on a line, ##.#0 mL, or halfway between two lines, ##.#5 mL).

8. Add the magnetic stir bar to the beaker containing the acid solution. Carefully place the beaker on the stir plate and turn the control knob to a setting where the stir bar is slowly spinning. Position the buret so that it is over the acid solution.

Notes on using the pH meter

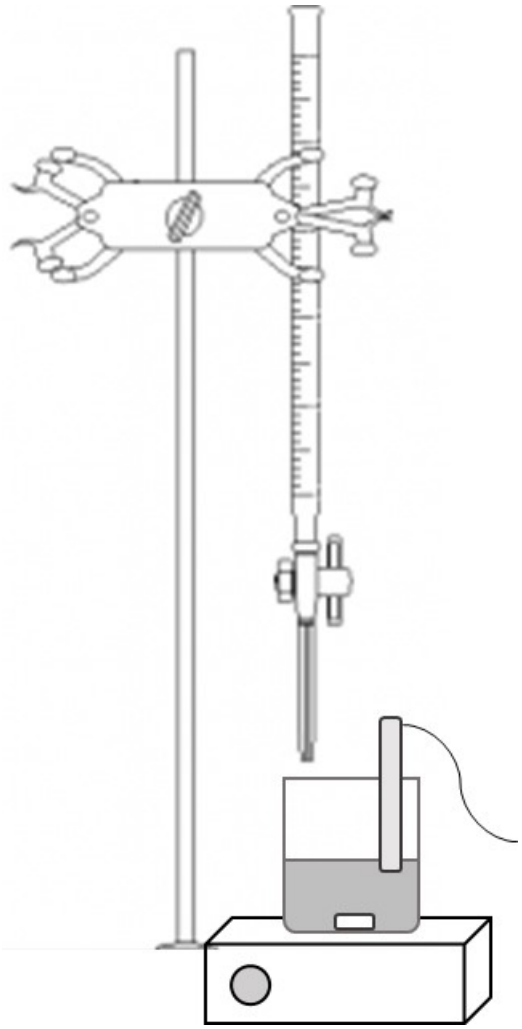
The pH probe should be kept in liquid. Do not let it sit out in air or to dry out.
Do not remove the probe from its holder (the "arm" on the pH meter).
Rinse the probe with deionized water between solutions to avoid contamination. Use your rinse bottle. Collect the rinse water in a labeled waste beaker.
When taking pH measurements, you must use the MANUAL MODE (see below).
All pH values should be recorded to two decimal places.

9. Calibrate the pH meter. Unless otherwise instructed, perform a two-point calibration using pH 7.00 and pH 10.00 buffers.

Borrow one of the small cups of each buffer from the reagent bench. Rinse the probe, place it into the first buffer, and press CAL. The reading on the pH meter should stabilize on the pH of the buffer.

Repeat with the second buffer. Return the cups of buffer that you borrowed to the reagent counter.

10. Rinse the probe and position it in the acid solution. Do not let the stir bar hit the tip of the probe.



11. Make sure that you have recorded the molarity of the NaOH from the reagent bottle to four decimal places and V_{in} from the buret to two decimal places.

12. Measure the initial pH of the acid solution. Use the pH meter in manual mode. Press READ on the pH meter. As the display on the pH meter blinks, count five seconds. Press READ again to freeze the pH value on the display. Record the pH to two decimal places.

For the titration, it is important to have sufficient data points, particularly near the equivalence point, to draw the curve. You may start with ~ 1 mL additions of NaOH, but you will need to reduce the volumes to ~0.5 mL and then go to drops. Do not remove the pH probe from the solution between NaOH additions.

13. Add ~ 1 mL NaOH from the buret to the beaker and press READ on the pH meter. Count 5 seconds while the display blinks and then press READ again to freeze the pH value shown. Record V_{buret} to two decimal places and the pH to two decimal places.

14. Repeat step 13 until the pH reaches ~4.70 – 4.80 (add-READ-count-READ-record).

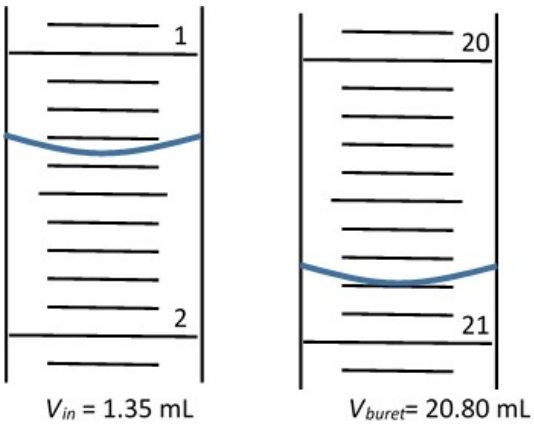
15. Repeat step 13 but transition to **~0.5 mL NaOH volumes** until the pH reaches ~5.30 – 5.40 (add-READ-count-READ-record).

16. Repeat step 13 but transition to **drops of NaOH** (add-READ-count-READ-record).

17. Once the pH jumps up to a pH >10.00, repeat step 13 but return to ~1 mL NaOH additions (add-READ-count-READ-record), making sure to get several data points after the pH stabilizes and flattens out at high pH (≥11.00).

You must use the add-READ-count-READ-record manual mode method.

$V_{OH^-\ added} = V_{buret} - V_{in}$ to two decimal places.



$V_{NaOH\ added}$ = 20.80 – 1.35 mL =19.45 mL

13. Prior to disposing of the titrated solution in the waste container, please carefully pull the stir bar out of the solution using the magnetic wand.

14. Wash all glassware well (tap water and soap, thorough tap water flush, and final deionized water rinse); please be very careful. Clean your work area. Return any equipment that you borrowed clean.

15. Repeat the titration but check with your TA to make sure you have enough time to complete it before you start.

16. When you have finished the experiment, including cleanup so that your work area looks at good if not better than when you started, plot pH vs. $V_{OH^-\ added}$ for each titration. The curves should look similar.

17. Identify V_{eq} and record its value to two decimal places. Use it to calculate the moles of HA titrated and the molar mass of HA (to four significant figures if $V_{eq} \geq 10.00$ mL; three if $V_{eq} < 10.00$ mL).

$$\mathrm{n_{OH^- added}} = \mathrm{n_{HA\ original}} = \left(\mathrm{V_{eq}}\ in\ L\right) \times \left(M_{\mathrm{OH^-}}\ in\ \frac{mol}{L}\right)$$

$$\mathrm{MM_{HA}} = \frac{\#\ \mathrm{g\ HA}}{\mathrm{mol\ HA}} = \frac{\mathrm{m_{HA}}\ in\ g\ from\ a\ balance\ measurement}{\mathrm{n_{HA\ total}}\ in\ mol\ from\ the\ titration\ curve\ analysis}$$

18. Determine the pK_a of HA to two decimal places from the pH at $^1/_2\,V_{eq}$ where pH ≈ pK_a.

Part 2. Melting point of the solid acid, T_m

Caution

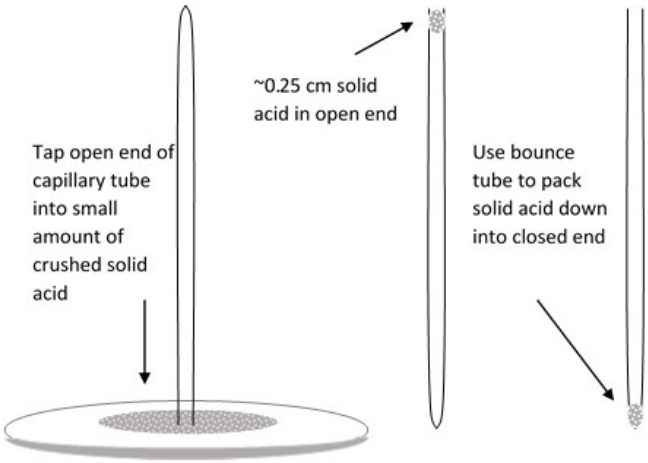
The capillary tubes (melting point tubes) are fragile. Please handle with care and dispose of used tubes in the solid waste container, not the trash or broken glass box.
The Meltemp apparatus gets hot inside. Do not reach into it.
Thermometers are not flexible and they will break if you try to bend them.

19. Obtain two capillary tubes, one for each T_m trial. Each sample can only be melted once.

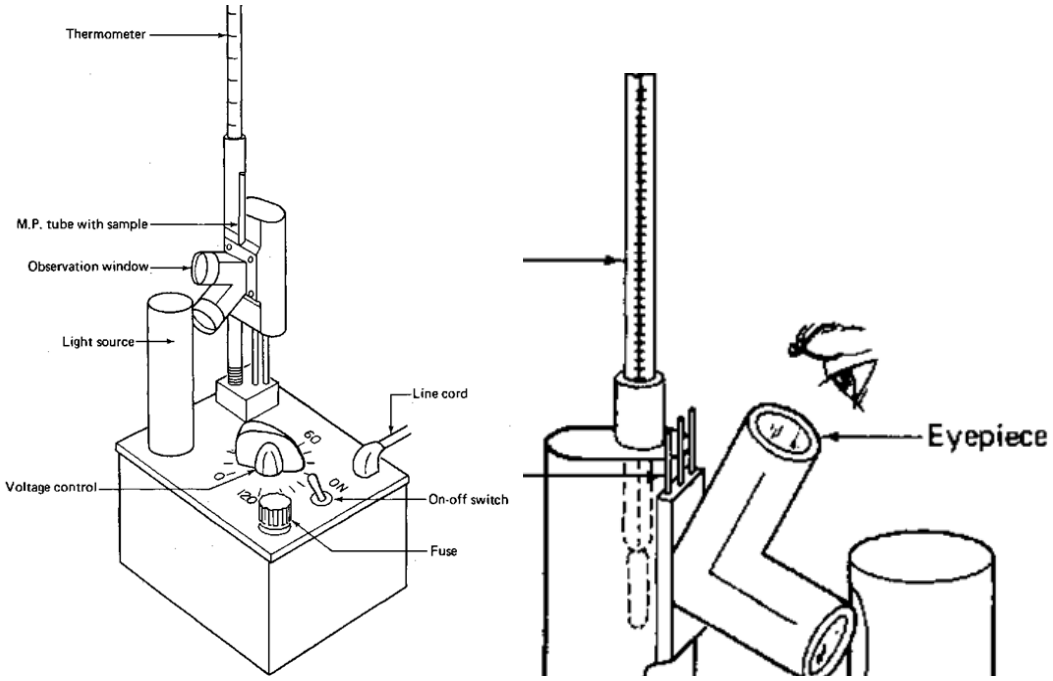
20. Pour a very small amount of the solid acid onto a watch glass. Using a piece of weigh paper to cover the solid, carefully crush the solid into a fine powder.

21. Tap the open end of a capillary tube into the crushed acid so that ~0.25 cm of the solid accumulates near the opening. You need just enough acid to see the phase change but too much will give a large melting point range.

22. Borrow a bounce tube (long glass tube). Hold the bounce tube so that it is resting on the lab bench. With the closed end down, drop the capillary tube down the bounce tube. You may have to do this several times, but the solid acid in the capillary tube should pack down to the closed end of the capillary tube.



23. Place one capillary tube into the Meltemp as instructed. You should be able to view the opaque solid acid in the tube through the window.



24. Use the voltage control to adjust the heating rate while watching both the temperature and the solid acid. Below ~80°C, a setting of ~5 should produce a satisfactory rise in temperature, but reduce the setting to ~2-3 above this temperature (these recommendations are approximate). The temperature should continue to increase but at a slower rate.

25. Watch the solid carefully. Record two temperatures to the ones place: a) $T_{first\ melt}$, where the solid first starts to melt (looks "sweaty"); and, b) $T_{all\ melt}$, where the solid is completely melted (goes "transparent"). The temperature range should be ~5°C or less. Report the melting point, T_m, as the average of $T_{first\ melt}$ and $T_{all\ melt}$.

26. Turn the Meltemp down. Carefully remove the used capillary tube and place it in the solid waste container.

Please follow your TA's instructions for cleanup and waste disposal. Return any equipment and glassware borrowed clean. Wash all glassware well (tap water and soap, tap water rinses, final deionized water rinse), being particularly careful with the buret.

Part 3. Identify the unknown acid

27. Calculate averages for $n_{OH^-\ added}$, $n_{HA\ original}$, MM_{HA}, pK_a, and T_m.

28. From the table, select the acid that most closely matches your experimental results.

Name of Acid	Molar Mass	pK_a	Melting Point (^oC)
acetylsalicylic	180.15	3.48	135
meta-aminobenzoic	137.13	4.78	175
ortho-aminobenzoic	137.13	6.97	145
para-aminobenzoic	137.13	4.92	187
benzoic	122.12	4.19	122
meta-chlorobenzoic	156.57	3.82	158
para-chlorobenzoic	156.57	3.98	243
d-lactic	90.08	3.83	52
ortho-nitrobenzoic	167.12	2.16	147
phenylacetic	136.14	4.25	77

Results / Sample Calculations

Complete the online inlab or write a lab report as directed by your TA.

Moles of OH^- at V_{eq}, moles HA, MM_{HA}, pK_a, T_m, and identity of HA

Discussion Questions and Review Topics

What did you find and how?
How closely did your experimental values match those of an acid in the table? How confident are you in your identification?
What were the major sources of error? How did the accuracy and precision of the equipment and techniques used affect your results?