Potentiometric titration of a HCl–H_3PO_4 mixture

Potentiometry will be used to detect the endpoints of the titration of a mixture containing unknown amounts of hydrochloric (strong) and phosphoric (weak polyprotic) acids. Your standardized NaOH will be used as titrant. A good understanding of the experimental logic will be needed to simultaneously analyze two components of a mixture. You will use a more advanced mathematical treatment of data – using first and second derivative graphs – to aid in the detection of the endpoints. You will be graded on your accuracy. This experiment is performed in pairs.

Required Reading
D.C. Harris***, Quantitative Chemical Analysis*** (7th ed., W. H. Freeman, NY, 2007) pp. 158–166, 180-183
Pipettes, ***Analytical Lab Manual***
Volumetric Flasks, ***Analytical Lab Manual***

PreLab Quiz Topics
In addition to being able to explain the purpose of your experiment, the general procedure steps, the use of all chemicals in this experiment and any specific hazards , your prelab quiz may include explanations of any of the following terms: strong and weak acid, polyprotic acid, pH, conjugate acids and bases, fraction of dissociation. You should be able to describe what you expect to see if you titrate a polyprotic acid with a strong base and know all relevant chemical reactions for this experiment. Describe the chemical and/or physical processes that will occur when you reach the endpoint of your titration. Explain how we can use first and second derivative analysis to determine the endpoints of your titrations. Explain how we can titrate a mixture and determine quantities of both components in a single titration.

Look up and record the three ionization steps of phosphoric acid in your notebook, along with their respective equilibrium constants. Because these equilibrium constants differ from each other by more than a factor of 10 000, there will be no more than two phosphate species present to any significant degree at any given pH. These two phosphate species will form a conjugate acid-base pair. As pH changes, protons are removed from (or added to) the phosphoric acid in a stepwise manner. The complete removal of each proton will be signaled by a distinct endpoint. We will observe two of the endpoints. These two endpoints are used to determine the phosphoric acid concentration by using the volume of standardized base needed to get from: 1) the start to the first endpoint, 2) from the first to the second endpoint, and 3) from the start to the second endpoint.

If a second acid (in our case, the strong acid HCl) is present in addition to the phosphoric acid, it will also react with base according to its equilibrium constant. The HCl proton and the first proton of H_3PO_4 will react with base simultaneously (HCl actually reacts first, but no distinct endpoint is observed). The result is that the volume of standard base used to reach the first endpoint represents the sum of the HCl and H_3PO_4 concentrations, while the volume of base used to get from the first endpoint to the second is

a measure of the H_3PO_4 concentration alone. From this information, the concentrations of both HCl and H3PO4 may be calculated. **This paragraph is important, if you don't understand it, read it again!**
The endpoints for this experiment cannot be easily detected using a visual (color) indicator; however, the endpoints are clear when you measure the potential of a suitable electrode as a function of titrant volume. You will measure the pH of the solution as a function of the volume of titrant added, using a combination pH electrode consisting of a glass indicator electrode and an Ag|AgCl electrode. A pH meter measures ***activity*** (i.e., p A_{H^+}), which can be converted into the actual concentration of hydrogen ions; however, during a titration all we care about is the location of inflection points. Whether we measure pH or A_{H^+}, the inflection points will occur at the same titrant volumes.

Chemicals and their Location

Fume Hood
Unknown Hydrochloric – Phosphoric acid mixture

Your Drawer
Sodium hydroxide, standardized soln

Equipment and its Location
Bench
LabPro unit with power supply, Drop Counter box , pH sensor
Magnetic stir plate

Safety Issues and Chemical Hazard Information

Hydrochloric acid water-reactive, corrosive toxic
Phosphoric acid corrosive none
Sodium hydroxide water-reactive, corrosive toxic, irritant

Both concentrated acids are highly corrosive. Be careful. Wear gloves while working with these chemicals.

Part 1. Preparing the equipment.

1. Put on your safety goggles.

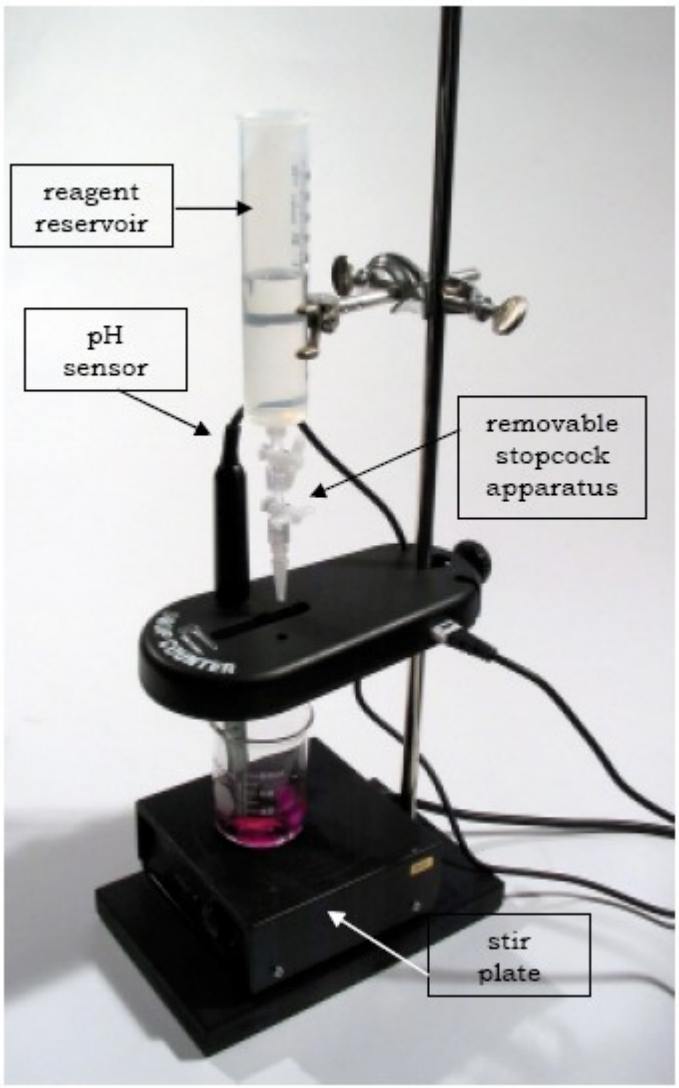
2. Obtain the following equipment
- a LabPro unit with power supply,
- a Drop Counter box
- a pH sensor
- USB cable

3. Turn on the computer and the LabPro unit.

4. Open the Drop Counter box. Take note of what is included in the box (the black drop counter, the reagent reservoir with removable stopcock apparatus, black microstirrer with silver circular magnet, cable with two white ends) and how it is packaged. You will need to return the box in excellent condition.

5. Attach the Drop Counter to a ring stand. (Eventually, you will place a stir plate under the Drop Counter.) Connect the cable with two white ends to both the Drop Counter and the LabPro in DIG/SONIC 1.

6. Attach the pH sensor to CH 1 of the LabPro. Pull the black pH sensor out of the storage solution. Insert the pH sensor through the large hole in the Drop Counter. Reinsert the pH probe into the storage solution.



8. Take the plastic reagent reservoir from the Drop Counter box. Attach the removable stopcock apparatus. Make sure all of the connections within the stopcock apparatus are tight. This setup includes two stopcocks. (**Note:** The bottom valve will be used to open or close the reservoir, while the top valve will be used to finely adjust the flow rate.) For now, close both stopcock valves by turning the handles to a horizontal position.

9. Rinse the plastic reagent reservoir with a few milliliters of your standardized NaOH solution. Pour/drain the waste into a **LABELED** NaOH waste beaker.

10. Use a clamp to attach the reagent reservoir to the ring stand. The reagent reservoir should be positioned so its tip is just above the long Drop Counter slot.

11. Make sure both stopcocks are closed, and then, fill the reagent reservoir with approximately 50 mL of the NaOH. (Do not allow the reservoir to overflow.)

12. Drain a small amount of NaOH solution into the labeled NaOH waste beaker, so it fills the reservoir's tip. (To do this, turn both valve handles to the vertical position for a moment, then turn them both back to horizontal.)

13. Open LoggerPro *by clicking on the icon on the desktop.*

14. If the message, "Connect to LabPro" opens and you are using a desktop, then you may need to check your USB connection, close LoggerPro, then reopen LoggerPro.

15. Prepare the computer for data collection by opening the file "24b Acid-Base (Drop Count)" from the *Chemistry with Computers* folder of Logger *Pro*.

a. Click on "File" on the menu at the top of the window.
b. Select "Open..."
c. Use the "Look in:" pull down menu to select "Local Disk (C:)".
d. Open the "Program Files" folder.
e. Open the "Vernier Software" folder.
f. Open the "Logger Pro 3" folder.
g. Open the "Experiments" file.
h. Open the "_Chemistry with Computers" folder.
i. Open the "24b Acid-Base (Drop Count)" file.

16. Calibrate the Drop Counter so that a precise volume of titrant is recorded in units of milliliters.

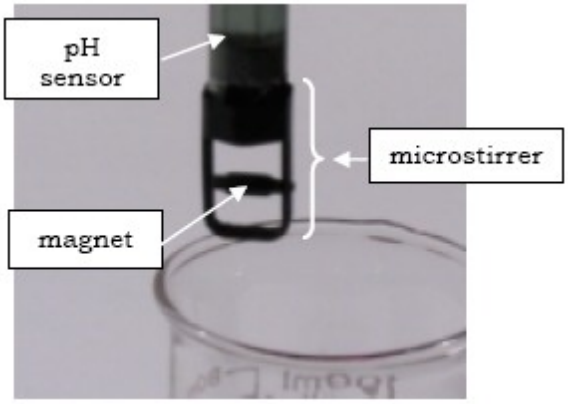
a. From the Experiment menu, choose Calibrate _ DIG 1: Drop Counter (mL).
b. Select the Automatic button.

c. Place a small beaker directly below the slot on the Drop Counter. (Be sure the beaker is aligned with the tip of the reagent reservoir.)

d. Open the bottom stopcock on the reagent reservoir by turning it vertical, while keep the top stopcock closed (horizontal).

e. Click the Start button.

f. Slowly open the top stopcock so that the drops are released at a slow rate (~1 drop per second). You should see the drops being counted on the computer screen. Your will use a Mohr pipet to measure the actual volume delivered.



1. Use a 25 mL volumetric pipette to transfer 25.0 mL of the unknown HCl-H3PO4 solution into a clean, dry, beaker, dilute the sample with 40 mL of distilled water.

2. Remove the storage solution from the pH sensor. Place the container in a safe location.

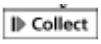
3. Use the DI water squirt bottle, the labeled NaOH waste beaker, and Kimwipes to rinse off the tip of the pH sensor, and then eliminate excess water.

4. Add the microstirrer to tip of the pH probe. Make sure the magnet can rotate completely and freely.

5. Place the acid solution on the stir plate (*No color indicator is used for this titration)*. Make sure the beaker is under the reagent reservoir. Insert the pH probe with microstirrer into the solution.

6. Turn on the stir plate so the microstirrer is stirring at a fast rate. Make sure the microstirrer is rotating completely and freely.

7. You are now ready to begin collecting data.

a. Click 

(No data will be collected until the first drop goes through the Drop Counter slot.)

b. Fully open the bottom valve—the top valve should still be adjusted so drops are released at a rate of about 1 drop every second.

c. When the first drop passes through the Drop Counter slot, check the data table to see that the first data pair was recorded.

8. Continue watching your graph to see when a large increase in pH takes place—this will be the first equivalence point of the reaction. Continue titrating in this way, until you have passed both endpoints and a negligible pH change is observed for each additional mL of titrant added. Then click 

. Turn the bottom stopcock of the reagent reservoir to a closed (horizontal) position.

9. Save your data, make sure you have Logger-Pro calculate both the first and second derivatives of the data. Save all data in a format that can be read with Excel.

Concentration determination

10. Go back and reread the introduction of this lab, to make sure you understand what is going on. The first endpoint is due to NaOH neutralizing both acids, but the second endpoint is due only to the neutralization of the phosphoric acid. (Note that both acids react 1:1 with NaOH.) For each titration run, use the volume of NaOH needed to titrate from the first endpoint to the second endpoint, to calculate the number of moles of NaOH that reacted with phosophoric acid at the second endpoint, and hence the number of moles of phosphoric acid in your unknown sample.

11. For each titration run, use the volume of NaOH needed to titrate to the first endpoint to calculate the number of moles of NaOH that reacted with both unknown acids at the first endpoint, and hence the total number of moles of acid in your unknown sample.

12. The amount of phosphoric acid is the same at both endpoints; i.e., the number of moles of phosphoric acid in your unknown found from the second endpoint will be equal to the number of moles of phosphoric acid in your unknown at the first endpoint. Thus, determine the number of moles of hydrochloric acid by subtracting the number of moles of phosphoric acid found from the second endpoint from the total number of moles of acid found from the first endpoint.

13. Knowing the volume of your unknown aliquot, and the number of moles of each of the two acids in your unknown aliquot, calculate the molarity of the two acids, HCl and H3PO4, in your unknown sample.

Discussion Questions

1. We didn't calibrate the pH meters before doing this experiment. Why doesn't this matter?
2. HCl has one proton and H3PO4 has three. We see only two endpoints. Which endpoints do we see and why don't we see four endpoints?
3. Explain clearly why we used a potentiometric titration for this analysis. Could we have used an indicator instead of a pH meter for this analysis?

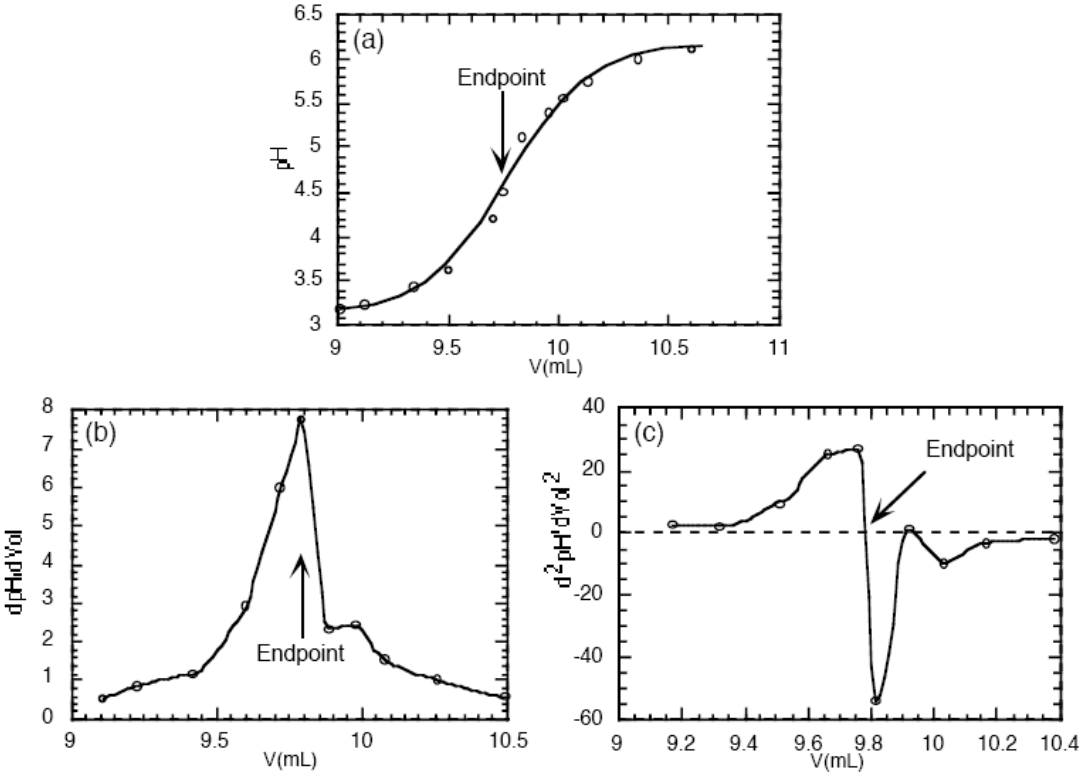
Data Analysis

Endpoint determination

The first derivative of a curve shows the slope of the curve. The slope of your titration curve should peak at each of the endpoints (~9.78 mL NaOH in the Figure part ***b***). Determine the two endpoints for each titration from your first derivative curves. Label the endpoints on your graphs

An alternative mathematical way to find the endpoints is to investigate the second derivative (d^2pH/dV^2), the rate of change for the slope of the curve. Make a new column in your spreadsheet and calculate d^2pH/dV^2 by dividing the change in dpH⁄dV between two consecutive readings, by the change in the average added volume between the two consecutive readings; e.g., The second derivative of a curve shows the rate of change of the slope of a curve, which should be equal to zero whenever the first derivative is at a maximum (or a minimum). At each endpoint, the second derivative should cross the x-axis, i.e., equal zero (~9.77 mL NaOH in the Figure part ***c***). The second derivative graph should give the most accurate determination of each endpoint. Determine the two endpoints for each titration from your second derivative curves. Label the endpoints on your graphs. (A good titration will have only a single crossing of the x-axis at each endpoint. If you have multiple crossings, use your best judgment to determine what value to choose.)

9. Use your graphs to determine your end point volumes as precisely as possible and explain how you chose them.



Sample potentiometric titration data analysis: (a) raw data, (b) first derivative curve, and (c) second derivative curve.