Lab 6. Use of Titration Curves to Determine the K_a of Two Weak Acids

Prelab Assignment

Before coming to lab:

- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" handout to complete in your lab notebook the following sections of the report for this lab exercise: Title, Introduction, Materials/Methods and Data Table (use the data table provided on page 6). An outline or flow chart of the procedure is appropriate for the Materials/Methods section. Ensure that the table of contents of your lab notebook is current.
- Read the lab thoroughly and answer the pre-lab questions that appear at the end of this lab exercise. Background information for this lab can be found in Chapter 19 in your textbook (*Silberberg* 5th ed).

Purpose

In this experiment you will titrate strong and weak acids, plot their titration curves, and find the K_a's for two weak acids, potassium hydrogen phthalate and maleic acid.

Introduction

Acid–base titration is a useful technique for determining the concentration of an acidic or basic solution. The titration of a weak acid or base is also useful for determining the K_a or K_b for an acid or base, respectively. You have already been introduced to titration techniques in previous laboratories.

In this experiment you will use a pH meter connected to a computer to generate plots of the titrations, called ***titration curves***. By plotting pH *vs* the volume of titrant the curve shows how the pH of the solution changes as an acid, or base, is added. The shape of a titration curve is influenced by both the concentration as well as the nature of the acid, or base. By titrating both strong and weak acids you will see different titration curves and how they change with the strength of the acid.

For this experiment you will perform three different titrations.

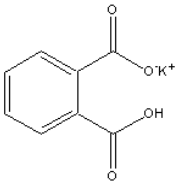
1. First, you will titrate a ***strong acid, HCl***, ***with a strong base, NaOH***. The concentration of the HCl will be known, and the results of the titration will allow you to calculate the concentration of the NaOH. The equation for the reaction is:

$$\mathbf{HCl_{(aq)} + NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)} + H_2O_{(l)}}$$

2. Secondly, you will titrate a ***weak acid, Potassium Hydrogen Phthalate*** (abbreviated KHP), ***with a strong base***. Phthalic acid is a weak, diprotic acid. On the other hand, KHP is the potassium salt of phthalic acid. Hence, *KHP is a weak monoprotic acid*. From the results of this titration you will be able to calculate the K_a for KHP. The equation here is:

$$\mathbf{KHP_{(aq)} + NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + K^{+}_{(aq)}\ P^{2-}_{(aq)} + H_2O_{(l)}}$$

Structure of KHP, potassium hydrogen phthalate



3. Lastly, you will titrate a ***weak diprotic acid***, Maleic Acid, $H_2C_4H_2O_4$, ***with a strong base***. The results of this titration will allow you to calculate K_a for the removal of each successive H+ ion in the acid—that is the acid dissociation constants for the first two reactions, below. It will also be interesting to compare the shape of the titration curves in the three cases. The individual and net equations are:

Removal of 1st Proton: $\mathbf{H_2C_4H_2O_{4(aq)} + NaOH_{(aq)} \rightarrow Na^+_{(aq)} + HC_4H_2O_4^-{}_{(aq)} + H_2O_{(l)}}$

Removal of 2nd Proton: $\mathbf{HC_4H_2O_4^-{}_{(aq)} + NaOH_{(aq)} \rightarrow Na^+_{(aq)} + C_4H_2O_4^{2-}{}_{(aq)} + H_2O_{(l)}}$

Net Equation: $\mathbf{H_2C_4H_2O_{4(aq)} + 2\ NaOH_{(aq)} \rightarrow 2\ Na^+_{(aq)} + C_4H_2O_4^{2-}{}_{(aq)} + 2\ H_2O_{(l)}}$

In all cases you will need to identify the equivalence point of the titration. The ***equivalence point*** is the point at which the number of moles of OH^- added to the solution equals the moles of H^+ originally present. The ***end point*** is the point where the indicator being used changes color. If the indicator is chosen correctly, the end point will essentially be exactly at the equivalence point.

The pH of the solution at the equivalence point depends on what is left in the flask once you have reached the equivalence point. *Before beginning the experiment think about what ions will be present at the endpoint in each titration, and decide whether you think the pH at the endpoint will be acidic, basic, or neutral*.

Titration Curves

To date the equivalence point of an acid base reaction has been determined using an indicator. In the last part of this experiment we are going to monitor the changes in pH that occurs during the titration of a weak diprotic acid with a strong base. At the equivalence point one should expect to see a dramatic change in pH as the solution goes from acidic to strongly basic.

Depicted in figure 1 is an idealized titration for a ***weak diprotic acid***.

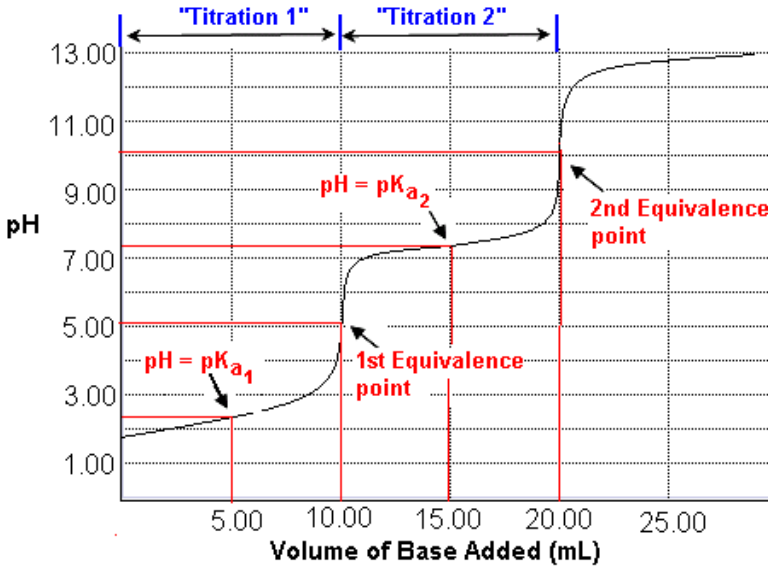


Figure 1. Titration Curve for a weak diprotic acid.

The first thing that you should notice is that there are two regions where we see a significant pH change. These, if you wish, correspond to two separate titrations. "Titration 1" is the reaction of the first proton with the base (in this case sodium hydroxide):

$$\mathbf{H_2X_{(aq)} + NaOH_{(aq)} \rightarrow NaHX_{(aq)} + H_2O_{(l)}}$$

and the "2nd titration" corresponds to the reaction of the second proton with sodium hydroxide:

$$\mathbf{NaHX_{(aq)} + NaOH_{(aq)} \rightarrow Na_2X_{(aq)} + H_2O_{(l)}}$$

In essence, the titration of a weak ***diprotic acid*** with a strong base such as sodium hydroxide is a combination of two titrations. Hence, the overall reaction for a weak diprotic acid is the *sum* of the two titrations:

$$\mathbf{H_2X_{(aq)} + 2NaOH_{(aq)} \rightarrow Na_2X_{(aq)} + 2H_2O_{(l)}}$$

In determining the quantity of the acid or the molarity of the acid, we are normally just interested in the final equivalence point. In a pH titration plot, this is determined by finding the point of inflection on the final area where we see a significant rise in pH (This can be approximated by determining the mid point.) However, this plot contains some other interesting features. First off, if we look at the area corresponding to the first titration, it should come as no surprise that its equivalence point corresponds to the addition of exactly half the volume of NaOH required to reach the final equivalence point. The real neat thing comes at the halfway point of each titration. Let us focus on the Titration 1. At the halfway point, the concentration of $H_2X(aq)$ remaining in the solution is equal to half the initial concentration of H_2X! The concentration of $NaHX(aq)$ produced is also numerically equal to half of the initial concentration of H_2X! So what, you may ask. Let's focus for a moment on the acid equilibrium associated with the acid that we are dealing with in titration 1.

$$\mathbf{H_2X_{(aq)} + H_2O_{(l)} \rightleftharpoons HX^-_{(aq)} + H_3O^+_{(aq)}}$$

$$K_a = \frac{[H_3O^+][HX^-]}{[H_2X]} \quad or \quad [H_3O^+] = \frac{K_a\,[H_2X]}{[HX^-]}$$

But at the ***halfway point of the titration*** the concentration of H_2X is exactly half of its initial concentration. Therefore at this point: $[H_2X] = [HX^-] = 0.5\,[H_2X]_{initial}$. Hence, at the halfway point of the titration…

$$[H_3O^+] = \frac{K_a \cdot 0.5[H_2X]_{initial}}{0.5[H_2X]_{initial}} \quad \text{or} \quad \mathbf{[H_3O^+] = K_a}$$

Taking the negative log of this yields: $\boldsymbol{pH = pK_a}$

From the titration curve we can determine the pH at the halfway point of the titration and thus determine the ***pKa*** of the acid! Moreover, since $\boldsymbol{pK_a = -\text{Log}\ K_a}$ we can determine the K_a of the acid. Neat! Since this is a diprotic acid, this corresponds to $\boldsymbol{K_{a1}}$. Guess what you can determine from the pH at the midpoint (***inflection point***) of the second titration? This information can be used to help identify the acid in question since K_a values for a large number of polyprotic acids are known.

*Procedure (*Work in teams of two.)

CAUTION !!!	***You will be handling strong acids and bases in this lab— You must wear goggles at all times.***

1. Obtain about 65–75 mL of NaOH and 30–35 mL of 0.10 *M* HCl.
2. Rinse a 50 mL buret with DI water and then rinse it a small amount (5 to 10 mL) the NaOH solution. Set up the buret on a ring stand with a buret clamp and then fill the buret with the NaOH to the 0.00 mL mark after expelling the air from the buret tip.
3. Obtain a pH probe from the lab cart. Clamp the probe on the ring stand of a Vernier magnetic stirrer so that you can move it up and down to insert it into solutions whose pH you want to measure—as shown in lab by the instructor.

CAUTION!!

- Be careful to handle the probe gently—the end where the potential of a solution is measured is ***quite fragile***.
- As you are working through these steps you should also take care to ***keep the probe moist at all times***.

4. After attaching the probe to the "Go!link", start the Logger Pro software. In the "Chemistry with Vernier" folder open the file "Exp 23 Titration Curves." The vertical axis has pH. If the horizontal axis is not labeled time in seconds and not "Volume (mL)" you will need to do the following:
    a. On the top menu bar just to the left of "Collect" click on the "data collection" icon.
    b. From the "Mode" pull down menu select "Events with Entry"
    c. Enter "Volume NaOH" next to "Column Name" and enter "Volume" next to "Short Name."
    d. Enter "mL" for units and then click "done."
    e. Now rescale the x-axis so the maximum volume is 30.00 mL by clicking on the 25.0 and entering 30.00.
5. Remove the probe from its storage container by unscrewing the top of the storage bottle and *leave the probe inside the bottle's lid* and calibrate the probe.
6. Use pH 4 and pH 7 buffer solutions to calibrate the pH probe as follows:
    a. Rinse the probe by squirting it with a small amount of deionized water, catching the runoff in a large beaker. Then gently pat the probe dry with a Kimwipe.
    b. Under "Experiment" on the upper menu bar select the "Calibrate" and then "Go!Link: pH 1." Insert the pH probe into the first buffer solution, click on "Calibrate Now", enter the pH of that buffer solution in the "Value 1" box, and click "Keep".
    c. Rinse and dry the probe again, insert it into a second buffer, enter the pH value of the buffer, click "Keep" and then "Done." You have now calibrated the probe!

Titration of a Strong Acid, HCl, with a Strong Base, NaOH

7. Pipet 25.00 mL of 0.10 *M* HCl into a 250 mL beaker. Add two drops of phenolphthalein to the beaker.
8. Position the HCl solution on a stir plate and below the buret. Position the pH electrode in the solution so that the stirring bar will ***not strike*** *the electrode*.
9. Before adding NaOH titrant click on the "Collect" button and monitor the pH for 5–10 seconds. Once the pH has stabilized, click on the "Keep" button. The computer will hold this pH value and wait for you to type in the buret reading. Enter the current buret reading—probably 0.00 mL. Click on the "OK" button. You have now saved the first data pair for this experiment.
10. You are now ready to begin the titration. This process goes more smoothly if one person manipulates and reads the buret while another person operates the computer and enters volumes. Your goal will be to generate enough data points to give a smooth curve. In some regions of the titration the pH changes very slowly and you can add several mL of base at a time. Nearer the endpoint, the pH changes very quickly and you will need to add base one drop at a time.

    Add the first increment of NaOH, enough to raise the pH about 0.20 units. When the pH stabilizes, again click on the "Keep" button and enter the current buret reading. Click on the "OK" button. You now have the second data pair.

    Continue adding NaOH solution in increments that raise the pH by about 0.20 units and enter the buret reading after each increment. When a pH of about 3.5 has been reached, change the increment of NaOH to single drops. Be sure to continue to enter the buret readings after each increment.

    When a pH of about 10 is reached again add larger increments that raise the pH by about 0.20 pH units, and input the buret reading after each increment. Continue adding NaOH solution until the pH remains constant.

11. The graph you have obtained is your titration curve. The endpoint is the volume at the steepest part of the curve. (If you've had calculus, this is also called the inflection point.) Determine the volume of NaOH needed to reach the endpoint (do this by selecting tangent function icon on the menu bar) and use this value to calculate the exact molarity of the NaOH. Print a copy of the titration curve for each student, as well as a copy of the data. **Note**: *You can save this file if you want to as the data will be lost when you do the next titration.*
12. ***Titration of a Weak Acid, Potassium Hydrogen Phthalate with NaOH:*** Repeat the procedure using a 25.00 mL sample of KHP instead of the HCl.
13. ***Titration of a Weak Diprotic Acid, Maleic Acid with NaOH:*** Repeat the procedure using a 25.00 mL sample of maleic acid.

Results

Team Members	Strong Monoprotic Acid with Strong Base			Weak Monoprotic Acid with Strong Base			Weak Diprotic Acid with Strong Base				
	Titration of 0.10 M HCl with NaOH			Titration of 0.10 M KHP with NaOH			Titration of 0.040 M Maleic Acid with NaOH				
								1st Equiv. Point		2nd Equiv. Point	
	Initial pH	Vol NaOH (mL)	pH at Equiv. Point	Initial pH	Vol NaOH (mL)	pH at Equiv. Point	Initial pH	Vol NaOH (mL)	pH	Vol NaOH (mL)	pH
Averages											

Analysis

1. From the results of the NaOH/HCl titration, calculate the molarity of the NaOH.
2. From the results of the NaOH/KHP titration, calculate K_a for KHP.
3. From the results of the NaOH/Maleic acid titration, calculate K_{a1} and K_{a2} for maleic acid.
4. Compare the shapes of the three titration curves. Describe the differences, and answer the following questions:
   a. Why is the curve for the HCl/NaOH titration so steep near the endpoint?
   b. Why does the curve for the NaOH/KHP titration change more slowly than in the HCl/NaOH case?
   c. Why does the curve for the NaOH/Maleic acid titration have two inflection points?
5. What is the pH at the endpoint of each titration? Clearly explain why each solution has a particular endpoint pH. Are these the pH's you predicted before starting the experiment?
6. What would the titration curve look like if 0.10 *M* NaOH were in the flask and 0.10 *M* HCl were in the buret? Make a rough sketch to illustrate your answer.

Labs 6 Prelab Questions **Name**_____

Titration Curves **Date** _____ **Section** _____ **Group No.**_____

Instructions: Complete the following questions and hand in at the start of your lab period or when instructed by your instructor. Show your work with units and correct significant figures for all questions that involve a calculation.

1. Predict the expected pH (<7, >7, =7) at the endpoint(s) of each of the three titrations. *Explain your reasoning*.
   a. Titration of a Strong Acid, HCl, with a Strong Base, NaOH

      Predicted pH (circle one): (a.) <7 (b.) 7 (c.) >7 *Circle your answer and explain below*.

   b. Titration of a Weak Acid, KHP, with a Strong Base, NaOH

      Predicted pH (circle one): (a.) <7 (b.) 7 (c.) >7 *Circle your answer and explain below*.

   b. Titration of a Weak Diprotic Acid, Maleic Acid, with a Strong Base, NaOH

      Predicted pH (circle one): (a.) <7 (b.) 7 (c.) >7 *Circle your answer and explain below*.

2. What volume of 0.025 M NaOH will be required to reach the endpoint in a titration with 25.00 mL of 0.10 M HCl? Show your work with units and correct significant figures. *Circle your answer*.

3. Calculate the molarity of a sodium hydroxide solution if 25.00 mL 0.100 M maleic acid requires 22.10 mL of NaOH to reach the endpoint. Show your work with units and correct significant figures. *Circle your answer*.