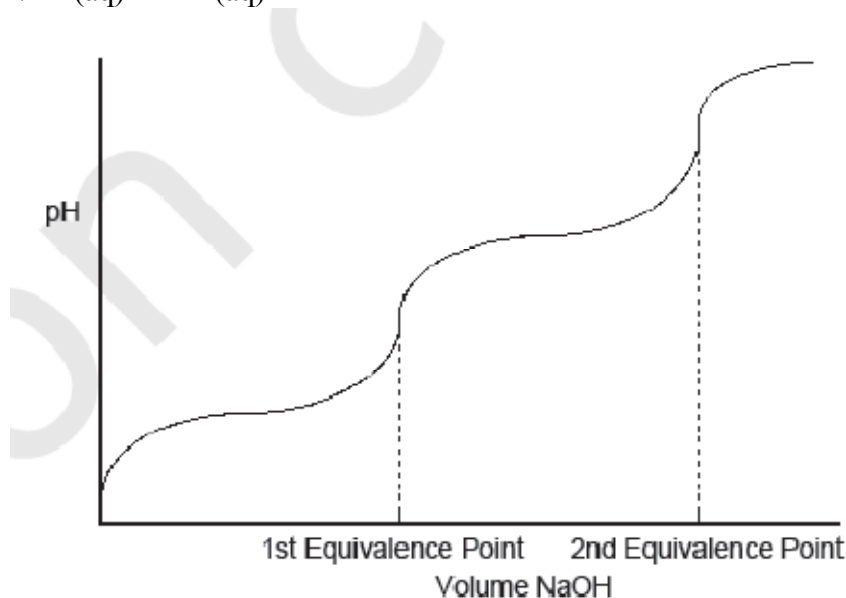
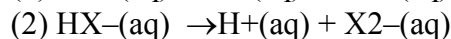


Titration of a Diprotic Acid: Identifying an Unknown

A diprotic acid is an acid that yields two H^+ ions per acid molecule. Examples of diprotic acids are sulfuric acid, H_2SO_4 , and carbonic acid, H_2CO_3 . A diprotic acid dissociates in water in two stages:



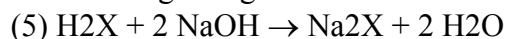
Because of the successive dissociations, titration curves of diprotic acids have two equivalence points, as shown in Figure 1. The equations for the acid-base reactions occurring between a diprotic acid, H_2X , and sodium hydroxide base, $NaOH$, are from the beginning to the first equivalence point:



from the first to the second equivalence point:



from the beginning of the reaction through the second equivalence point (net reaction):



At the first equivalence point, all H^+ ions from the first dissociation have reacted with $NaOH$ base.

At the second equivalence point, all H^+ ions from *both* reactions have reacted (twice as many as at the first equivalence point). Therefore, the volume of $NaOH$ added at the second equivalence point is exactly twice that of the first equivalence point (see Equations 3 and 5). The primary purpose of this experiment is to identify an unknown diprotic acid by finding its molecular weight. A diprotic acid is titrated with $NaOH$ solution of known concentration.

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Molecular weight (or molar mass) is found in g/mole of the diprotic acid. Weighing the original sample of acid will tell you its mass in grams. Moles can be determined from the volume of NaOH titrant needed to reach the first equivalence point. The volume and the concentration of NaOH titrant are used to calculate moles of NaOH. Moles of unknown acid equal moles of NaOH at the first equivalence point (see Equation 3). Once *grams* and *moles* of the diprotic acid are known, molecular weight can be calculated, in g/mole. Molecular weight determination is a common way of identifying an unknown substance in chemistry.

You may use either the first or second equivalence point to calculate molecular weight. The first is somewhat easier, because moles of NaOH are equal to moles of H₂X (see Equation 3). If the second equivalence point is more clearly defined on the titration curve, however, simply divide its NaOH volume by 2 to confirm the first equivalence point; or from Equation 5, use the ratio: 1 mole H₂X / 2 mol NaOH

OBJECTIVE

In this experiment, you will identify an unknown diprotic acid by finding its molecular weight.

MATERIALS

Materials for *both* Method 1 (buret) and Method 2 (Drop Counter)

- 1) magnetic stirrer
- 2) stirring bar
- 3) Logger *Pro* wash bottle
- 4) pH Sensor
- 5) distilled water
- 6) unknown diprotic acid,
- 7) 0.120 g ring stand
- 8) ~0.1 M NaOH solution (standardized)
- 9) 1 utility clamp
- 10) milligram balance
- 11) 250 mL beaker

Materials required *only* for Method 1 (buret)

- 1) 50 mL buret
- 2) 2nd utility clamp
- 3) 2nd 250 mL beaker

Materials required *only* for Method 2 (Drop Counter)

- 1) Drop Counter
- 2) 100 mL beaker
- 3) 60 mL reagent reservoir
- 4) 10 mL graduated cylinder

CHOOSING A METHOD

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Method 1 has the student deliver volumes of NaOH titrant from a buret. After titrant is added, and pH values have stabilized, the student is prompted to enter the buret reading manually and a pH-volume data pair is stored.

Method 2 uses a Drop Counter to take volume readings. NaOH titrant is delivered drop by drop from the reagent reservoir through the Drop Counter slot. After the drop reacts with the reagent in the beaker, the volume of the drop is calculated, and a pH-volume data pair is stored.

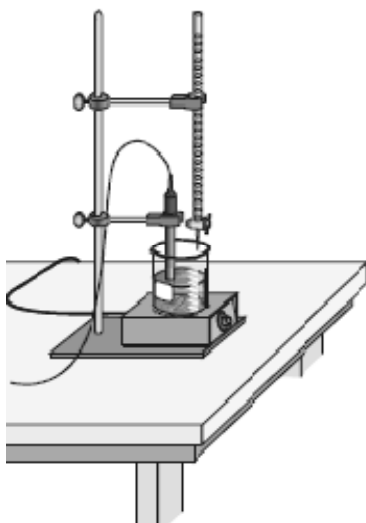
METHOD 1: Measuring Volume Using a Buret

- 1) Obtain and wear goggles.
- 2) Weigh out about 0.120 g of the unknown diprotic acid on a piece of weighing paper. Record the mass to the nearest 0.001 g in your data table. Transfer the unknown acid to a 250 mL beaker and dissolve in 100 mL of distilled water. **CAUTION:** *Handle the solid acid and its solution with care. Acids can harm your eyes, skin, and respiratory tract.*
- 3) Place the beaker on a magnetic stirrer and add a stirring bar. If no magnetic stirrer is available, you need to stir with a stirring rod during the titration.
- 4) Use a utility clamp to suspend a pH Sensor on a ring stand as shown here. Position the pH Sensor in the diprotic acid solution and adjust its position toward the outside of the beaker so it will not be struck by the stirring bar. Turn on the magnetic stirrer, and adjust it to a medium stirring rate (with no splashing of solution).
- 5) Obtain approximately 60 mL of ~0.1 M NaOH solution in a 250 mL beaker. Obtain a 50 mL buret and rinse the buret with a few mL of the ~0.1 M NaOH solution. Record the precise concentration of the NaOH solution in your data table. Use a utility clamp to attach the buret to the ring stand. Fill the buret a little above the 0.00 mL level of the buret. Drain a small amount of NaOH solution into the beaker so it fills the buret tip *and* leaves the NaOH at the 0.00 mL level of the buret. Dispose of the waste solution from this step as directed by your teacher. **CAUTION:** *Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing.*
- 6) You are now ready to begin the titration. This process goes faster if one person manipulates and reads the buret while another person operates the computer and enters buret readings.
 - a. Before adding NaOH titrant, click and monitor pH for 5-10 seconds. Once the pH has stabilized, click . In the edit box, type "0" (for 0 drops added), and press ENTER to store the first data pair for this experiment.
 - b. Add enough NaOH to raise the pH by about 0.20 units. When the pH stabilizes, again click . In the edit box, type the current buret reading, to the nearest 0.01 mL. Press ENTER. You have now saved the second data pair for the experiment.
 - c. Continue adding NaOH solution in increments that raise the pH about 0.20 units and enter the buret reading after each addition. Proceed in this manner until the pH is 3.5.
 - d. When pH 3.5 is reached, change to 2-drop increments. Enter the buret reading after each increment.
 - e. After pH 4.5 is reached, again add larger increments that raise the pH by about 0.20 units and enter the buret reading after each addition. Continue in this manner until a pH of 7.5 is reached.

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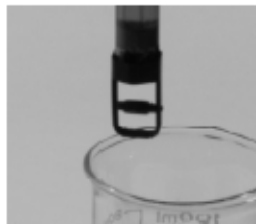
- f. When pH 7.5 is reached, change to 2-drop increments. Enter the buret reading after each increment.
 - g. When pH 10 is reached, again add larger increments that raise the pH by 0.20 units. Enter the buret reading after each increment. Continue in this manner until you reach a pH of 11.
- 7) When you have finished collecting data, click . Dispose of the beaker contents as directed by your teacher.
 - 8) Print a copy of the table. Then print a copy of the graph.

METHOD 2: Measuring Volume with a Drop Counter



- 1) Obtain and wear goggles.
- 2) Connect the pH Sensor to CH 1 of the computer interface. Lower the Drop Counter onto a ring stand and connect its cable to DIG/SONIC 1.
- 3) Weigh out about 0.120 g of the unknown diprotic acid on a piece of weighing paper. Record the mass to the nearest 0.001 g in your data table. Transfer the unknown acid to a 100 mL beaker and dissolve in 40 mL of distilled water. **CAUTION:** *Handle the solid acid and its solution with care. Acids can harm your eyes, skin, and respiratory tract.*
- 4) Obtain approximately 40 mL of ~0.1 M NaOH solution in a 250 mL beaker. Record the precise NaOH concentration in your data table. **CAUTION:** *Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing.*
- 5) Obtain the plastic 60 mL reagent reservoir. **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 valves by turning the handles to a horizontal position.
- 6) Rinse it with a few mL of the ~0.1 M NaOH solution. Use a utility clamp to attach the reagent reservoir to the ring stand. Add the remainder of the NaOH solution to the reagent reservoir.
- 7) Drain a small amount of NaOH solution into the 250 mL beaker so it fills the reservoir's tip.

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- 8) To do this, turn both valve handles to the vertical position for a moment, then turn them both back to horizontal.



- 9) Prepare the computer for data collection by opening the file “25b Titration (Drop Count)” from the *Chemistry with Computers* folder. Check to see that the pH value is between 1.5 and 2.5.
- 10) To calibrate drops so that a precise volume of titrant is recorded in units of milliliters:
- From the Experiment menu, choose Calibrate _ DIG 1: Drop Counter (mL).
 - Proceed by one of these two methods:
 - If you have previously calibrated the drop size of your reagent reservoir and want to continue with the same drop size, select the Manual button, enter the number of Drops / mL, and click . Then proceed directly to Step 8.
 - If you want to perform a new calibration, select the Automatic button, and continue with Step c below.
 - Place a 10 mL graduated cylinder directly below the slot on the Drop Counter, lining it up with the tip of the reagent reservoir.

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- d. Open the bottom valve on the reagent reservoir (vertical). Keep the top valve closed (horizontal).
 - e. Slowly open the top valve of the reagent reservoir so that drops are released at a slow rate
 - f. (~1 drop every two seconds). You should see the drops being counted on the computer screen.
 - g. When the volume of NaOH solution in the graduated cylinder is between 9 and 10 mL, close the bottom valve of the reagent reservoir.
 - h. Enter the precise volume of NaOH (read to the nearest 0.1 mL) in the edit box. Record the number of Drops / mL displayed on the screen for possible future use.
 - i. Discard the NaOH solution in the graduated cylinder as indicated by your instructor and set the graduated cylinder aside.
- 11) Assemble the apparatus.
- a. Place the magnetic stirrer on the base of the ring stand.
 - b. Insert the pH Sensor through the large hole in the Drop Counter.
 - c. Attach the Microstirrer to the bottom of the pH Sensor, as shown here. Rotate the paddle wheel of the Microstirrer and make sure that it does not touch the bulb of the pH Sensor.
 - d. Adjust the positions of the Drop Counter and reagent reservoir so they are both lined up with the center of the magnetic stirrer.
 - e. Lift up the pH Sensor, and slide the beaker containing the HCl solution onto the magnetic stirrer. Lower the pH Sensor into the beaker.
 - f. Adjust the position of the Drop Counter so that the Microstirrer on the pH Sensor is just touching the bottom of the beaker.
 - g. Adjust the reagent reservoir so its tip is just above the Drop Counter slot.
 - h. Turn on the magnetic stirrer so that the Microstirrer is stirring at a fast rate.
 - i. You are now ready to begin collecting data. Click . No data will be collected until the first drop goes through the Drop Counter slot. Fully open the bottom valve—the top valve should still be adjusted so drops are released at a rate of about 1 drop every 2 seconds. When the first drop passes through the Drop Counter slot, check the data table to see that the first data pair was recorded.
- 12) Continue watching your graph to see when a large increase in pH takes place—this will be the equivalence point of the reaction. Then, a second large increase occurs at the second equivalence point. When this jump in pH occurs, let the titration proceed for several more milliliters of titrant, then click . Turn the bottom valve of the reagent reservoir to a closed (horizontal) position.
- 13) Dispose of the beaker contents as directed by your teacher.
- 14) Print copies of the table. Then print copies of the graph.

EQUIVALENCE POINT DETERMINATION: An Alternate Method

An alternate way of determining the precise equivalence point of the titration is to take the first and second derivatives of the pH-volume data. The equivalence point volume corresponds to the *peak* (maximum) value of the first derivative plot, and to the volume where the second derivative equals *zero* on the second derivative plot.

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- 1) In Method 1, view the first-derivative graph ($\Delta\text{pH}/\Delta\text{vol}$) by clicking the on the vertical-axis label (pH), and choose First Derivative. You may need to autoscale the new graph by clicking the Autoscale button,
- 2) In Method 2, you can also view the first derivative graph (pH/ Δvol) on Page 2 of the experiment file by clicking on the Next Page button, . On Page 2 you will see a plot of first derivative vs. volume.
- 3) In Method 1, view the second-derivative graph ($\Delta^2\text{pH}/\Delta\text{vol}^2$) by clicking on the vertical-axis label, and choosing Second Derivative. In Method 2, view the second-derivative on Page 3 by clicking on the Next Page button,

PROCESSING THE DATA

- 1) On your printed graph, one of the two equivalence points is usually more clearly defined than the other; the two-drop increments near the equivalence points frequently result in larger increases in pH (a steeper slope) at one equivalence point than the other. Indicate the more clearly defined equivalence point (first or second) in your data table.
- 2) Use your graph and data table to determine the volume of NaOH titrant used for the equivalence point you selected in Step 1. To do so, examine the data to find the largest increase in pH values during the 2-drop additions of NaOH. Find the NaOH volume just *before* this jump. Then find the NaOH volume *after* the largest pH jump. Underline both of these data pairs on the printed data table and record them in your data table.
- 3) Determine the volume of NaOH added at the equivalence point you selected in Step 1. To do this, add the two NaOH volumes determined in Step 2, and divide by two. For example: $12.34 + 12.44 \div 2 = 12.39 \text{ mL}$
- 4) Calculate the number of moles of NaOH used at the equivalence point you selected in Step 1.
- 5) Determine the number of moles of the diprotic acid, H₂X. Use Equation 3 or Equation 5 to obtain the ratio of moles of H₂X to moles of NaOH, depending on which equivalence point you selected in Step 1.
- 6) Using the mass of diprotic acid you measured out in Step 1 of the procedure, calculate the molecular weight of the diprotic acid, in g/mol.
- 7) From the following list of five diprotic acids, identify your unknown diprotic acid.

Diprotic Acid	Formula	Molecular weight
Oxalic Acid	H ₂ C ₂ O ₄	90
Malonic Acid	H ₂ C ₃ H ₂ O ₄	104
Maleic Acid	H ₂ C ₄ H ₂ O ₄	116
Malic Acid	H ₂ C ₄ H ₄ O ₅	134
Tartaric Acid	H ₂ C ₄ H ₄ O ₆	150

- 8) Determine the percent error for your molecular weight value in Step 6.
- 9) For the *alternate* equivalence point (the one you did *not* use in Step 1), use your graph and data table to determine the volume of NaOH titrant used. Examine the data to find the largest increase in pH values during the 2-drop additions of NaOH. Find the NaOH volume just before and after this jump. Underline both of these data pairs on the printed data table and record them in the Data and Calculations table. Note: Dividing or

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multiplying the other equivalence point volume by two may help you confirm that you have selected the correct two data pairs in this step.

- 10) Determine the volume of NaOH added at the alternate equivalence point, using the same method you used in Step 3.
- 11) On your printed graph, clearly specify the position of the equivalence point volumes you determined in Steps 3 and 10, using dotted reference lines like those in Figure 1. Specify the NaOH volume of each equivalence point on the horizontal axis of the graph.

DATA TABLE

Mass of diprotic acid	g
Concentration of NaOH	M
1. Equivalence point (indicate which one you will use in the calculations below)	first equivalence point ___ or second equivalence point ___
2. NaOH volume added before and after the largest pH increase	_____ mL _____ mL
3. Volume of NaOH added at the equivalence point	mL
4. Moles of NaOH	mol
5. Moles of diprotic acid, H ₂ X	mol
6. Molecular weight of diprotic acid	g/mol
7. Name, formula, and accepted molecular weight of the diprotic acid	_____ g/mol
8. Percent error	%
9. Alternate equivalence point (indicate the one used in the calculations below)	first equivalence point ___ or second equivalence point ___
10. NaOH volume added before and after the largest pH increase	_____ mL _____ mL
11. Volume of NaOH added at the alternate equivalence point	mL

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