Experiment
25

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:

(1) $H_2X(aq) \longleftrightarrow H^+(aq) + HX^-(aq)$

(2) $HX^-(aq) \longleftrightarrow H^+(aq) + X^{2-}(aq)$

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:

(3) $H_2X + NaOH \longleftrightarrow NaHX + H_2O$

from the first to the second equivalence point:

(4) $NaHX + NaOH \longleftrightarrow Na_2X + H_2O$

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

(5) $H_2X + 2\ NaOH \longleftrightarrow Na_2X + 2\ H_2O$

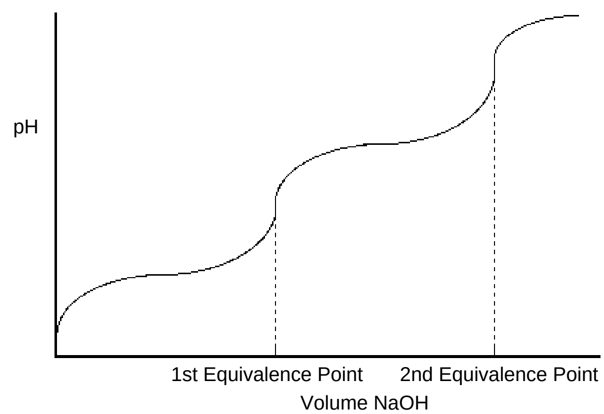


Figure 1

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. 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 H_2X (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:

$$1 \text{ mole } H_2X / 2 \text{ mol NaOH}$$

OBJECTIVE

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

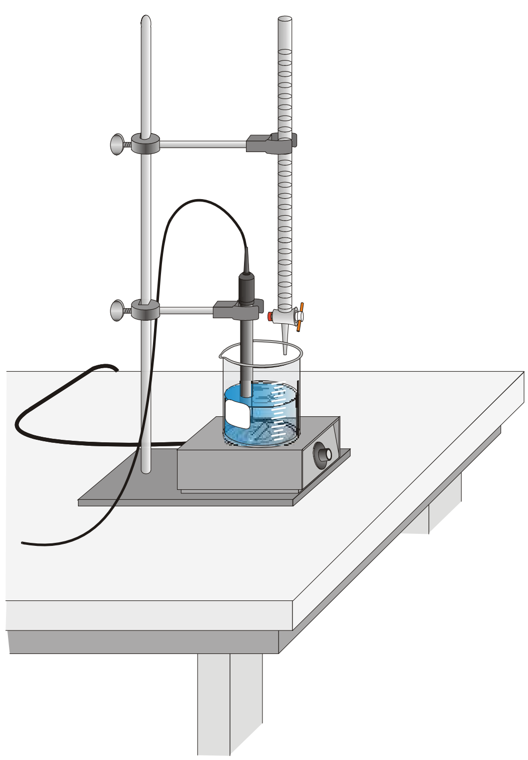
MATERIALS

- computer
- Vernier computer interface
- Logger *Pro*
- Vernier pH Sensor
- unknown diprotic acid, 0.120 g
- ~0.1 M NaOH solution (standardized)
- milligram balance
- 50 mL buret
- 2nd 250 mL beaker (or larger)
- magnetic stirrer
- stirring bar or Vernier Microstirrer
- wash bottle
- distilled water
- ring stand
- 1 utility clamp
- 250 mL beaker
- 2nd utility clamp

PROCEEDURE

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.

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. Connect the pH Sensor to the computer interface. Prepare the computer for data collection by opening the file "25a Titration Dip Acid" from the *Chemistry with Computers* folder of Logger *Pro*.

7. 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 **Collect** and monitor pH for 5-10 seconds. Once the pH has stabilized, click **Keep**. 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 **Keep**. 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.
   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.

8. When you have finished collecting data, click **Stop**. Dispose of the beaker contents by flushing them down the drain with running water.

9. Print a copy of the table. Then print a copy of the graph. Attach both to your lab report.

REPORT SHEET

Name____Date___________________________Period___

PROCESSING THE DATA (SHOW CALCULATIONS IN TABLE)

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. Show your work in the table. To do this, add the two NaOH volumes determined in Step 2, and divide by two. For example:

$$\frac{12.34 + 12.44}{2} = 12.39 \text{ mL}$$

4. Calculate the number of moles of NaOH used at the equivalence point you selected in Step 1. Show your work in the table.

5. Determine the number of moles of the diprotic acid, H_2X. Use Equation 3 or Equation 5 to obtain the ratio of moles of H_2X to moles of NaOH, depending on which equivalence point you selected in Step 1. Show your work in the table.

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. Show your work in the table.

7. From the following list of five diprotic acids, identify your unknown diprotic acid.

Diprotic Acid	Formula	Molecular weight
Oxalic Acid	$H_2C_2O_4$	90
Malonic Acid	$H_2C_3H_2O_4$	104
Maleic Acid	$H_2C_4H_2O_4$	116
Malic Acid	$H_2C_4H_4O_5$	134
Tartaric Acid	$H_2C_4H_4O_6$	150

8. Determine the percent error for your molecular weight value in Step 6. Show your work in the table.

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 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. Show your work in the table.

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 & CALCULATIONS TABLES

Mass of diprotic acid	g
Concentration of NaOH	M

1. Equivalence point (indicate with a check mark ✓ 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 (Show work here)	mL
4. Moles of NaOH (Show work here)	mol
5. Moles of diprotic acid, H_2X (Show work here)	mol

6. Molecular weight of diprotic acid (Show work here)	g/mol
7. Name, formula, and accepted molecular weight of the diprotic acid	__________ __________ ______ g/mol
8. Percent error. Include equation for full credit. (Show work here)	%

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

EXTRA CREDIT

Using a half-titration method, it is possible to determine the acid dissociation constants, K_{a1} and K_{a2}, for the two dissociations of the diprotic acid in this experiment. The K_a expressions for the first and second dissociations, from Equations 1 and 2, are:

$$K_{a1} = \frac{[H^+][HX^-]}{[H_2X]} \qquad K_{a2} = \frac{[H^+][X^{2-}]}{[HX^-]}$$

The first half-titration point occurs when *one-half* of the H^+ ions in the first dissociation have been titrated with NaOH, so that $[H_2X] = [HX^-]$. Similarly, the second half-titration point occurs when one-half of the H^+ ions in the second dissociation have been titrated with NaOH, so that $[HX^-] = [X^{2-}]$. Substituting $[H_2X]$ for $[HX^-]$ in the K_{a1} expression, and $[HX^-]$ for $[X^{2-}]$ in the K_{a2} expressions, the following are obtained:

$$K_{a1} = [H^+] \qquad K_{a2} = [H^+]$$

Taking the base-ten log of both sides of each equation,

$$\log K_{a1} = \log[H^+] \qquad \log K_{a2} = \log[H^+]$$

Thus, the pH value at the first half-titration volume, Point 1 in Figure 2, is equal to the pK_{a1} value. The first half-titration point volume can be found by dividing the first equivalence point volume by two.

Similarly, the pH value at the second titration point, is equal to the pK_{a2} value. The second half-titration volume (Point 2 in Figure 2) is midway between the first and second equivalence point volumes (1st EP and 2nd EP). Use the method described below to determine the K_{a1} and K_{a2} values for the diprotic acid you identified in this experiment.

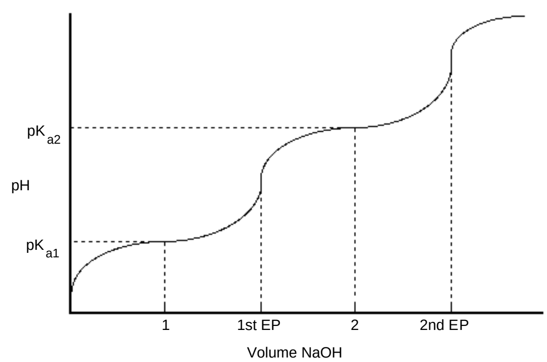


Figure 2

1. Determine the precise NaOH volume for the *first* half-titration point using one-half of the first equivalence point volume (determined in Step 2 or Step 9 of Processing the Data). Then determine the precise NaOH volume of the *second* half-titration point halfway between the first and second equivalence points.

2. On your graph of the titration curve, draw reference lines similar to those shown in Figure 2. Start with the first half-titration point volume (Point 1) and the second half-titration point volume (Point 2). Determine the pH values on the vertical axis that correspond to each of these volumes. Estimate these two pH values to the nearest 0.1 pH unit. These values are the pK_{a1} and pK_{a2} values, respectively. (Note: See if there are volume values in your data table similar to either of the half-titration volumes in Step 1. If so, use their pH values to confirm your estimates of pK_{a1} and pK_{a2} from the graph.)

3. From the pK_{a1} and pK_{a2} values you obtained in the previous step, calculate the K_{a1} and K_{a2} values for the two dissociations of the diprotic acid.