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

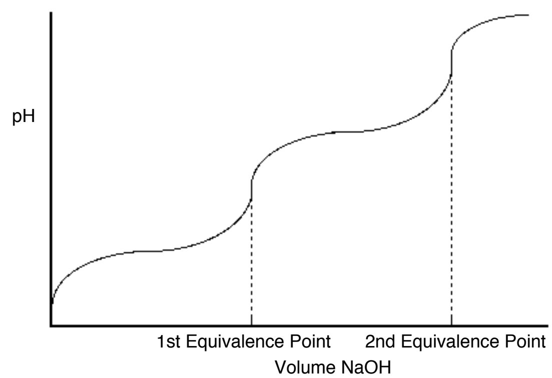

Figure 1

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:

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

MATERIALS

- LabPro or CBL 2 interface
- TI Graphing Calculator
- DataMate program
- pH Sensor
- unknown diprotic acid, 0.120 g
- milligram balance
- ~0.1 M NaOH solution
- 50-mL buret
- magnetic stirrer (if available)
- stirring bar
- ring stand
- 2 utility clamps
- 250-mL beaker
- wash bottle
- distilled water

PROCEDURE

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 the Data and Calculations 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.

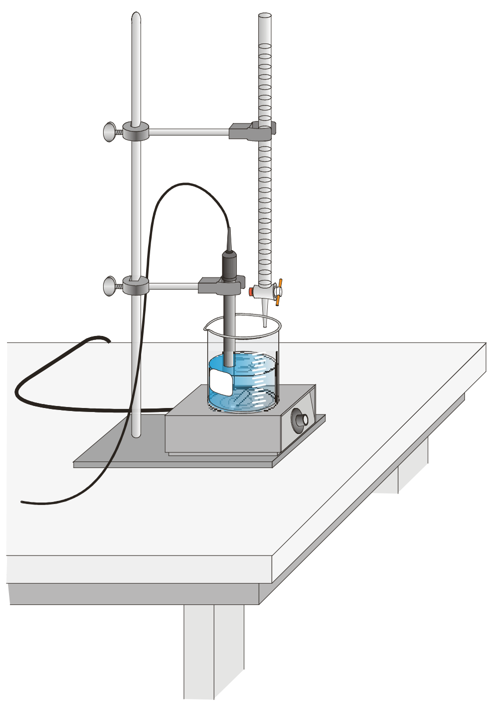

Figure 2

4. Plug the pH Sensor into Channel 1 of the LabPro or CBL 2 interface. Use the link cable to connect the TI Graphing Calculator to the interface. Firmly press in the cable ends.

5. Use a utility clamp to suspend a pH Sensor on a ring stand as shown in Figure 2. Position the pH electrode in the diprotic acid solution and adjust its position toward the outside of the beaker so that it is not struck by the stirring bar.

6. 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 the Data and Calculations table. Use a utility clamp to attach the buret to the ring stand as shown in Figure 2. Fill the buret a little above the 0.00-mL level of the buret. Drain a small amount of NaOH solution so it fills the buret tip *and* leaves the NaOH at the 0.00-mL level of the buret. Dispose of the waste solution in this step as directed by your teacher. **CAUTION:** *Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing.*

7. Turn on the calculator and start the DATAMATE program. Press [redacted] to reset the program.

8. Set up the calculator and interface for the pH Sensor.
   a. Select SETUP from the main screen.
   b. If CH 1 displays PH, proceed directly to Step 9. If it does not, continue with this step to set up your sensor manually.
   c. Press [redacted] to select CH 1.
   d. Select PH from the SELECT SENSOR menu.

9. Set up the data-collection mode.
   a. To select MODE, press ▲ once and press [redacted].
   b. Select EVENTS WITH ENTRY from the SELECT MODE menu.
   c. Select OK to return to the main screen.

10. You are now ready to perform the titration. This process goes faster if one person manipulates and reads the buret while another person operates the calculator and enters volumes.
   a. Select START to begin data collection.
   b. Before you have added any NaOH solution, press [redacted] and type in “0” as the buret volume in mL. Press [redacted] to save the first data pair for this experiment.
   c. Add the next increment of NaOH titrant (enough to raise the pH about 0.20 units). When the pH stabilizes, press [redacted] and enter the current buret reading (to the nearest 0.01 mL). You have now saved the second data pair for the experiment.
   d. Continue adding NaOH solution in increments that raise the pH by about 0.20 units and enter the buret reading after each increment. Proceed in this manner until the pH is 3.5.
   e. When pH 3.5 is reached, change to 2-drop increments. Enter the buret reading after each increment.
   f. 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.
   g. When pH 7.5 is reached, change to 2-drop increments. Enter the buret reading after each increment.
   h. 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 or use 25 mL of NaOH, whichever comes first.

11. Press STO▶ when you have finished collecting data.

12. Examine the data on the displayed graph to find the *equivalence point*—that is the largest increase in pH upon the addition of 1 drop of NaOH solution. As you move the cursor right

or left on the displayed graph, the volume (X) and pH (Y) values of each data point are displayed below the 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 Box 1 of the Data and Calculations table. Determine the volume of NaOH titrant used for the equivalence point you selected. 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. Record these values in Box 2 of your data table.

For the *alternate* equivalence point (the one you did *not* use in the previous step), examine the data points on your graph 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. Record these values in Box 10 of your data table.

13. Dispose of the beaker contents as directed by your teacher. Rinse the pH Sensor and return it to the pH storage solution.

14. Before printing the graph of pH *vs.* volume, rescale the y axis from 0 to 12 pH units, with increments of 1 pH unit. To do this:
    a. Press [redacted] to return to the main screen.
    b. Select GRAPH from the main screen.
    c. Press [redacted], then select RESCALE.
    d. Select Y SCALE from the RESCALE menu.
    e. Enter "0" as the minimum pH (Ymin).
    f. Enter "12" as the maximum pH (Ymax).
    g. Enter "1" as the pH increment (Yscl). The y-axis on the displayed graph should now have pH scaled from 0 to 12, with increments of 1 pH unit.

15. Print a copy of the graph of pH *vs*. volume.

16. (optional) Using Graphical Analysis software, print a copy of the NaOH volume and pH data for the titration.

PROCESSING THE DATA

1. Use your graph and data table to confirm the volumes you recorded in Box 2 of the Data and Calculations table (volumes of NaOH titrant *before* and *after* the largest increase in pH values). Underline both of these data pairs on the printed data table.

2. 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 1, and divide by two.

3. Calculate the number of moles of NaOH used at the equivalence point you selected in Step 1.

4. 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.

5. Using the mass of diprotic acid you measured in Step 1 of the procedure, calculate the molecular weight of the diprotic acid, in g/mol.

6. 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

7. Determine the percent error for your molecular weight value in Step 5.

8. Use your graph (and data table, if you printed one) to confirm the volumes you recorded in Box 10 of the Data and Calculations table (volumes of NaOH titrant *before* and *after* the largest increase in pH values at the alternate equivalence point). Underline both of these data pairs on the printed data 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.

9. Determine the volume of NaOH added at the alternative equivalence point, using the same method you used in Step 2 of Processing the Data.

10. On your printed graph, clearly specify the position of the equivalence point volumes you determined in Steps 2 and 9, 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	mL

1. Equivalence point (indicate which one you will use 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_2X	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

EXTENSION

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 3, 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 3) 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.

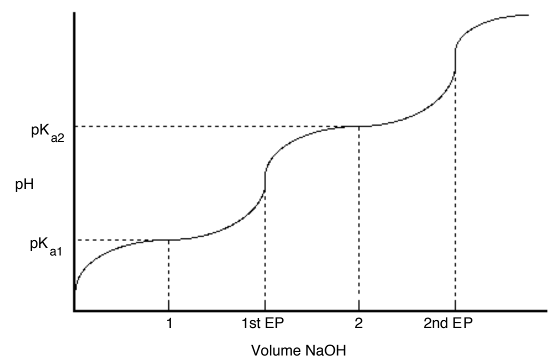

Figure 3

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 3. 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.