CHM 152 LL,
Determining the Identity of an Unknown Diprotic Acid

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) $H_2A(aq) \longleftrightarrow H^+(aq) + HA^-(aq)$
(2) $HA^-(aq) \longleftrightarrow H^+(aq) + A^{2-}(aq)$

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_2A, and sodium hydroxide base, NaOH, are from the beginning to the first equivalence point:

(3) $H_2A + NaOH \longleftrightarrow NaHA + H_2O$

from the first to the second equivalence point:

(4) $NaHA + NaOH \longleftrightarrow Na_2A + H_2O$

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

(5) $H_2A + 2\ NaOH \longleftrightarrow Na_2A + 2\ H_2O$

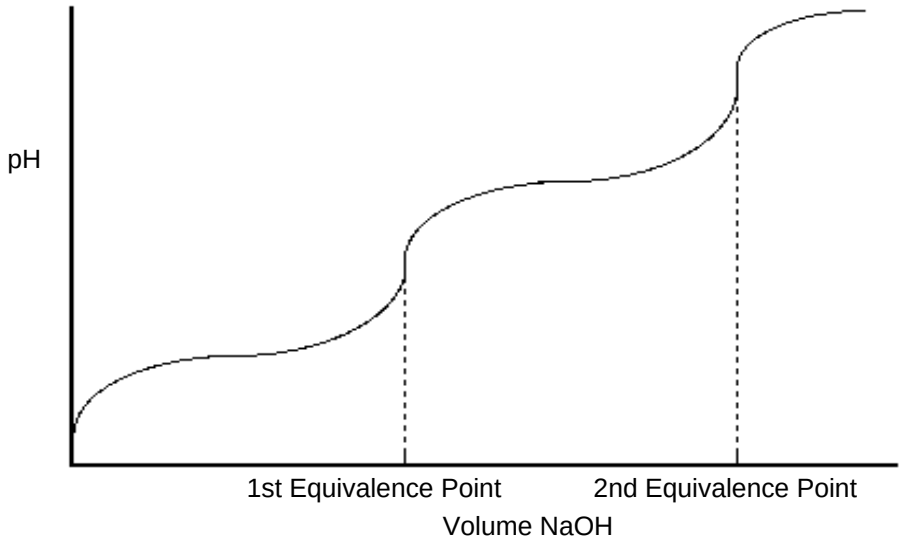

Figure 1

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).

Standardization of NaOH Solution (Week #1)

In this experiment, you will titrate a known mass of standard potassium hydrogen phthalate, KHP, with a basic sodium hydroxide solution, NaOH. Hydrogen ions from the KHP react with hydroxide ions from the NaOH in a one-to-one ratio to produce water in the overall reaction:

$$H^+(aq) + P^{2-}(aq) + K^+(aq) + Na^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + K^+(aq) + Na^+(aq) + P^2(aq)$$

When a KHP solution is titrated with an NaOH solution, the pH of the acidic solution is initially low. As base is added, the change in pH is quite gradual until close to the equivalence point, when equimolar amounts of acid and base have been mixed. Near the equivalence point, the pH increases very rapidly, as shown in Figure 2. The change in pH then becomes more gradual again, before leveling off with the addition of excess base.

In this experiment, you will use a computer to monitor pH as you titrate. The region of most rapid pH change will then be used to determine the equivalence point. The volume of NaOH titrant used at the equivalence point will be used to determine the molarity of the NaOH.

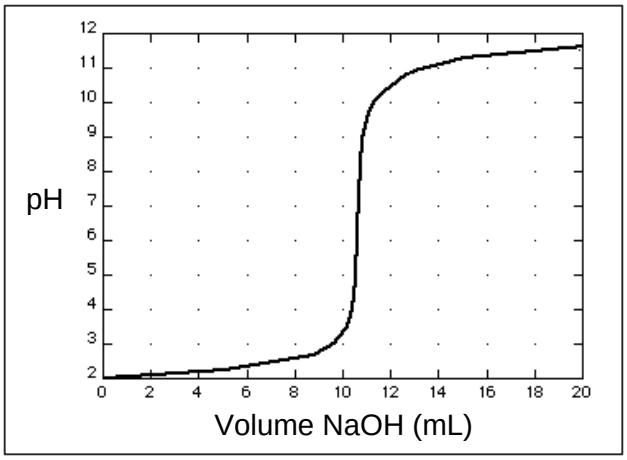

Figure 2

MATERIALS:

Windows PC	~0.1 M NaOH solution
Vernier Computer Interface	potassium hydrogen phthalate
Logger Pro software	stirring bar
Vernier pH Sensor	ring stand
unknown diprotic acid, 0.120 g	utility clamp and buret clamp
analytical balance	250-mL beaker
distilled water	wash bottle
50 mL buret	phenolphthalein (optional)

PROCEDURE:

1. Obtain and wear goggles.
2. Weigh out about 0.250 g of the potassium hydrogen phthalate on a piece of weighing paper. Record the mass to the nearest 0.0001 g in the Data and Calculations table of your packet. Transfer the KHP standard 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.

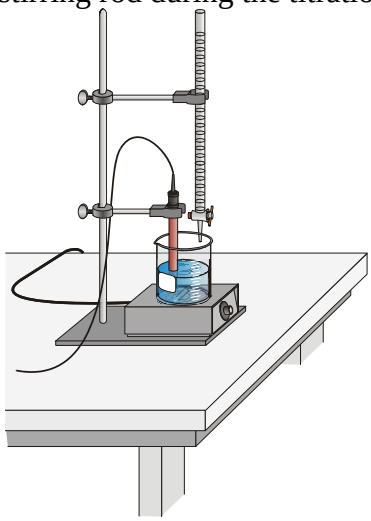

Figure 3

4. Use a utility clamp to suspend a pH Sensor on a ring stand as shown in Figure 3. Position the pH Sensor in the KHP solution and adjust its position toward the outside of the beaker so that it is not struck by the stirring bar.

4a. [Optional]. Place a few drops of phenolphthalein in the reaction mixture as a color change indicator signaling the reaction end point.

5. 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 or a buret clamp to attach the buret to the ring stand as shown in Figure 3. 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 from this step as directed by your teacher. CAUTION: *Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing.*
6. **Equipment Setup**
   a. Connect the *Vernier Logger Pro* interface to the computer, turn on the interface, and turn on the computer.
   b. Connect the pH sensor's DIN plug to Channel A on the interface.
   c. Prepare the computer for data collection by opening the file "07a Acid-Base" from the *Advanced Chemistry with Computers* folder. The Vernier file has a digits display, a Table display, and a Graph display of pH versus volume.

7. **pH Sensor Calibration**.
   First Calibration Point
   a. Choose Calibrate CH1: pH from the Experiment menu and then click "Calibrate Now" button.
   b. Remove the sensor from the bottle by loosening the lid, then rinse the sensor with distilled water. Dap dry on a Kimwipe.
   c. Place the sensor tip into the pH-7 buffer. Type "7" (the pH value of the buffer) in the edit box.
   d. When the displayed voltage reading for Reading 1 stabilizes, click Keep button.
   Second Calibration Point
   e. Rinse the sensor with distilled water, dap dry and place it in the pH-10 buffer solution.
   f. Type "10" (the pH value of the buffer) in the edit box.
   g. When the displayed voltage reading for Reading 2 stabilizes, click Keep button, then click the "Done" button.
   (Alternative: Vernier pH-BTA sensors usually need no calibration. Possible exceptions: water quality, Ka chemistry labs, or older pH sensors.
   - as of 1/2005, PH-BTA is individually calibrated (each sensor has a unique factory slope and intercept)
   - using Logger *Pro* program, you can store your custom calibrations directly to PH-BTA sensor, by choosing Calibrate->pH from the Experiment menu, then pull-down Live Calibration and choose Calibration Storage. Click on Write Calibration to Sensor, and follow the on-screen instructions.)
8. 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.
   Before adding NaOH titrant, click the Collect button and monitor pH for 5-10 seconds. Note that the Collect button has changed to a Keep button. The live Meter window below the graph should show a pH value between 1.5 and 2.5.
   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.
   - Add enough NaOH to raise the pH by about 0.15 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.
   - Continue adding NaOH solution in increments that raise the pH about 0.15 units and enter the buret reading after each addition. Proceed in this manner until the pH is 3.5.
   - When pH 3.5 is reached, change to 1-drop increments (or a quick turn demonstrated by the instructor). Enter the buret reading after each increment. [NOTE:] It is important that all increment volumes in this part of the titration be equal; that is one-drop increments.
   - After a pH value of approximately 10 is reached, again add larger increments that raise the pH by about 0.15 units and enter the buret reading after each addition.
   - Continue in this manner until the pH value remains constant.
9. When you have finished collecting data, click Stop. Dispose of the beaker contents as directed by your teacher.

10. Print a copy of the Table window. Enter your name(s) and the number of copies of the table.
11. If a printer is available, print a copy of the Graph window. Enter your name(s) and the number of copies of the graph.

PROCESSING THE DATA: (Standardization of NaOH Solution)

1. Determine the volume of NaOH added to reach the equivalence point. To do this, the equivalence point volume may be easily determined by examining a graph of the first derivative vs. volume ($\Delta pH/\Delta vol$). To obtain the derivative of your graph, select the points by clicking and dragging over the equivalence point region, then click on the "Statistics Menu" button and drag down to the "Derivative" function. The highest point on the graph of the derivative vs. volume plot is the equivalence point.
2. Recall that you massed approximately 0.2500 g of the standard KHP (molar mass = 204.23 g) solution for each titration. Calculate the number of moles of KHP used.
3. See the equation for the neutralization reaction given in the introduction. Determine the number of moles of NaOH used.
4. Calculate the molarity of the NaOH solution. Record the value in your lab packet.

[5]. If time permits, you may perform additional trial titrations, and then determine the average concentration of the NaOH solution. Alternatively, the average of the class results may be used.

Determining the Identity of the Diprotic Acid (Week #2)

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_2A (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 H_2A / 2 mol NaOH

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 0.0001 g in the Data and Calculations Table. Transfer the unknown acid quantitatively to a 250 mL beaker and dissolve the acid 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. Repeat procedural steps #3-11in the "Standardization of NaOH Solution" portion of the experiment.

PROCESSING THE DATA:

Diprotic Acid Identification

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 the Data and Calculations Table.
2. Determine the volume of NaOH added to reach the equivalence point. To do this, the equivalence point volume may be easily determined by examining a graph of the first derivative vs. volume ($\Delta pH/\Delta vol$). To obtain the derivative of your graph, select the points by clicking and dragging over the more clearly defined equivalence point region, then click on the "Statistics Menu" button and drag down to the "Derivative" function. The highest point on the graph of the derivative vs. volume plot is the equivalence point.
3. Calculate the number of moles of NaOH used at the equivalence point you selected in Processing the Data Step 2.
4. Determine the number of moles of the diprotic acid, H_2A. Use Equation 3 or Equation 5 to obtain the ratio of moles of H_2A to moles of NaOH, depending on which equivalence point you selected in Processing the Data Step 2.
5. Using the mass of diprotic acid you measured out in Procedure Step 2, 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 and record your decision on the Data and Calculations Table.

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. Ask the instructor for the identity of your unknown and then calculate the percent error for your molecular weight value determined in Step 5.

Determination of Ka_1 and Ka_2

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:

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} \qquad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

The first half-titration point occurs when *one-half* of the H^+ ions in the first dissociation have been titrated with NaOH, so that $[H_2A] = [HA^-]$. If we substitute $[H_2A]$ for $[HA^-]$ in the K_{a1} expression under these conditions, then $K_{a1} = [H^+]$.

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 $[HA^-] = [A^{2-}]$. If we substitute $[HA^-]$ for $[A^{2-}]$ in the K_{a2} expression, then under these conditions, $K_{a2} = [H^+]$.

Taking the negative log of both sides of each equation,

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

Therefore, pKa_1 = pH at the half-titration point for equivalence point 1.
Therefore, pKa_2 = pH at the half-titration point for equivalence point 2

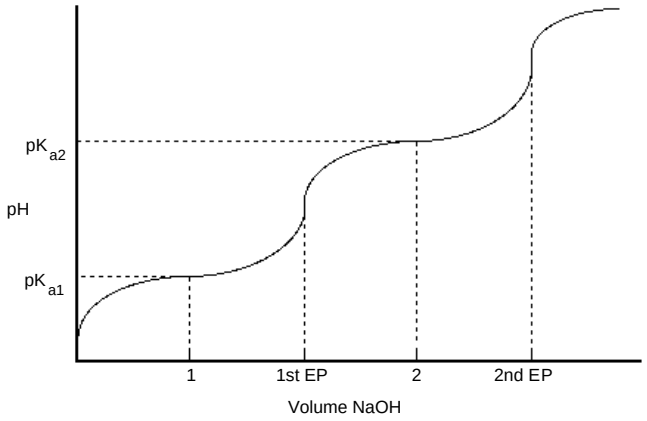

Figure 4

Thus, the pH value at the first half-titration volume, Point 1 in Figure 4, 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 4) 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.

1. On your graph of the titration curve, draw reference lines similar to those shown in Figure 4. 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.)
2. 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 and record these in the Data and Calculations Table.

Name _____ Section _____

CHM 152LL, Determining the ID of an Unknown Diprotic Acid

DATA AND CALCULATIONS TABLE for Standardization of NaOH.

	Trial #1	**Trial #2**
Mass of KHP (grams)		
Moles KHP		
Moles of NaOH		
Volume of NaOH added at equivalence point (mL)		
Concentration of NaOH (Molar) **Average Concentration of NaOH (Molar)**		

DATA TABLE for Diprotic Acid Experiment

Mass of diprotic acid	**g**
Concentration of NaOH	**M**

Equivalence point (indicate which one you will use you will use in the calculations below)	**first equivalence point ____** **second equivalence point ____**
Volume of NaOH added at the equivalence point	**_____mL**
Moles of NaOH	
Moles of diprotic acid, H_2A	
Molecular weight of diprotic acid	**g/mol**
Name, formula, and accepted molecular weight of the assigned diprotic acid	**_____** **_____** **_____ g/mol**
Percent error	**%**
Ka_1	
Ka_2	

Compare your results with the accepted values for the assigned acid and discuss potential sources of experimental error.