Determination of the Equivalent Weight and the K_a or K_b for a Weak Acid or Base

INTRODUCTION

Chemists frequently make use of the equivalent weight (eq. wt.) as the basis for volumetric calculations. The meaning of equivalent weight can change depending upon the type of reaction which serves as the basis for analysis, i.e., neutralization, oxidation-reduction, precipitation, or complex formation. Furthermore, it should be noted that the chemical behavior of a substance must be carefully specified if its equivalent weight is to be unambiguously defined.

The equivalent weight of a substance involved in a neutralization (acid/base) reaction is defined as that weight which reacts with or contributes 1 gram formula weight of hydrogen ion in that reaction. This is discussed at some length in your textbook.

In this experiment, you will be given a compound which is either a pure weak acid or a pure weak base. You are asked to determine the nature of the substance (i.e. is it an acid or a base?), its equivalent weight, and its dissociation constant. If possible, using the values you obtain and the CRC Handbook, identify your compound.

REAGENTS

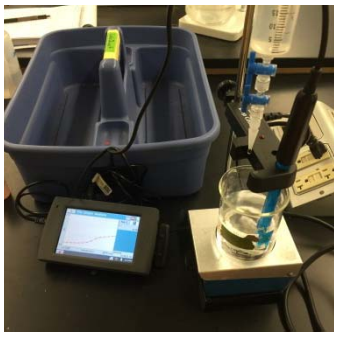
Ethanol, phenolphthalein and methyl red indicators are provided for you.

PROCEDURE

1. Obtain your unknown weak acid or base, and dry it as instructed to do so if it is a solid.
2. To determine the nature of your compound: Dissolve a small amount of your unknown in water. If you find your unknown to be rather insoluble in water, try heating the solution. If this also proves unsuccessful, you will need to switch to a 10% ethanol/water mixture. Using Litmus paper determine whether your unknown is an acid or base. Likewise, Hydrion paper may be used.
3. If your compound is a weak acid, you will need to prepare a standard (ca. 0.1M) solution of NaOH for titration. If your compound is a weak base, you will need a standard (ca. 0.1M) solution of HCl to titrate your unknown sample.
4. Perform a “quick and dirty” titration to get an estimate of the equivalent weight of your unknown. Weigh out a small amount (~0.5 g) of your unknown and dissolve it in 50 mL of water (or appropriate solvent) in a 250 mL Erlenmeyer flask. Add 2-3 drops of indicator (phenolphthalein for an acid, methyl red for a base), and titrate the sample to the appropriate endpoint.
5. Determination of the equivalent weight. Using the results of the quick and dirty titration, estimate the mass of unknown that would require ~40 mL of titrant to reach the endpoint. Accurately weigh out 3-4 samples of this mass of your unknown (separately). Dissolve each in 50 mL of solvent in 250-mL Erlenmeyer flasks. Add 2-3 drops of indicator, titrate and then calculate the equivalent weight of your unknown.

6. Next you will collect titration curve data to determine the dissociation constant for your unknown. You will use a computer-based data acquisition system to collect this data. The procedure below outlines the use of this system. Before acquiring the hardware for the measurement, weigh out enough (to the nearest 0.1 mg) of your unknown to require ~ 50 mL of titrant into a 250 mL beaker (not an Erlenmeyer flask!). Dissolve the sample as you found necessary before in ~100 mL of solvent. If you heat your solution, let it cool to room temperature before titrating. If you wish to use an indicator for this titration, use phenolphthalein for an acidic unknown, methyl red for one that is basic. An indicator is not essential for this titration, since you are monitoring the pH of the solution with the meter, but it is interesting to watch how the color change correlates with change in pH.

7. Procedure for using a LabQuest interface to determine titration curve and export data that can be analyzed in LoggerPro. (Portions adapted from the Vernier website). See Appendix 1 on page 5 for instructions for using a computer and LoggerPro interface for data collection.



NOTE: If you are unfamiliar with the LoggerPro system, please read the Introduction to LoggerPro 3 available at chemlab.truman.edu.

A. Connect the pH Sensor to CH 1 of the LabQuest interface. Lower the Drop Counter onto a ring stand and connect its cable to DIG 1.

B. Turn the LabQuest on (if you have not already done so). The interface should recognize the presence of both the pH sensor and drop counter. If the sensors are not recognized, consult your instructor.

C. Obtain the plastic 60 mL reagent reservoir. Close both valves by turning the handles to a horizontal position. Follow the steps below to set up the reagent reservoir for the titration.

   1. Rinse the reagent reservoir with a few mL titrant.
   2. Use a utility clamp to attach the reservoir to the ring stand.
   3. Fill the reagent reservoir with slightly more than 60 mL of the titrant (the exact volume isn't critical.
   4. Place a waste beaker beneath the tip of the reservoir and drain a small amount of the titrant into beaker so that it fills the reservoir's tip, then close both valves.

D. Calibrate the drops that will be delivered from the reagent reservoir

   1. From the "Sensors" menu on the LabQuest, choose "Calibrate" and select the Drop Counter.
   2. Place a 10 mL graduated cylinder directly below the slot on the Drop Counter, lining it up with the tip of the reagent reservoir.
   3. Open the bottom valve on the reagent reservoir (vertical). Keep the top valve closed (horizontal). Tap "Calibrate Now".

4. Slowly open the top valve of the reagent reservoir so that drops are released at a slow rate (~1 drop every second or two). You should see the drops being counted on the LabQuest screen. If you don't see this, consult your instructor.
5. When the volume of the titrant solution in the graduated cylinder is between 9 mL and 10 mL, close the **bottom** valve of the reagent reservoir.
6. Enter the precise volume of titrant solution (read to the nearest 0.1 mL) in the edit box. Also record the number of Drops/mL displayed on the screen in your notebook. Tap "OK"

E. Calibrate the pH sensor using two pH buffers (7 and 4 if titrating with base or 7 and 10 if titrating with acid)
1. From the "Sensors" menu on the LabQuest, select "Calibrate" and choose the pH Sensor.
2. Immerse the pH Sensor in the pH 7 buffer. Tap "Calibrate Now". Observe the value under "Live voltage", once it has stabilized, enter 7.00 for "Value 1" and tap "Keep"
3. Remove the pH sensor from the pH 7 buffer, rinse it with distilled water, and immerse it into the second buffer. ". Observe the value under "Live voltage", once it has stabilized, enter the corresponding pH for "Value 2" and tap "Keep"
4. Tap "OK" to exit the calibration routine. The pH sensor is now ready for use. It should be removed from the buffer solution and placed into your unknown solution.

F. Assemble the apparatus
1. Place the magnetic stirrer on the base of the ring stand.
2. Insert the pH Sensor through the large hole in the Drop Counter.
3. Lift up the pH Sensor, and place the beaker containing the unknown solution onto the magnetic stirrer. Lower the pH Sensor into the beaker.
4. Place a small magnetic stir bar in the solution, making sure that it does not touch the bulb of the pH Sensor. Adjust the position of the Drop Counter as necessary.
5. Adjust the reagent reservoir so its tip is just above the Drop Counter slot.
6. Turn on the magnetic stirrer so that the stir bar is stirring at a moderate rate.

G. You are now ready to begin collecting data. Tap the green "Collect" arrow on the bottom left of the screen. 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 1-2 seconds. When the first drop passes through the Drop Counter slot, check the data table to see that the first data pair was recorded.

H. Continue collecting data until you observe a plateau in the pH. When the reaction is complete, turn the bottom valve of the reagent reservoir to a closed (horizontal) position. Titrate until no appreciable change in pH occurs (about pH 12 if adding NaOH or pH 2 if

adding HCl). This should put you well past the end point. Tap the red "Stop" button on the bottom left of the screen.

I. Use the LabQuest File menu to save your data on the LabQuest. For further data analysis, you will need to either e-mail the file to yourself or transfer the file to a USB thumb drive (or both if you are a little paranoid!).

   a. To e-mail the file to yourself, you must first log in to the wireless network. Tap on the Wi-Fi icon next to the battery icon on the bottom right of the screen. Tap on the "gear" icon on the top right side of the screen that appears to open the Network Settings screen. On the Network Settings screen, select the TrumanSecureWireless network and use your Truman credentials to log in. Once you are logged in, tap "OK" and tap the "X" in the connections window to return to the data screen. From the data screen, tap "File" and select "Email" and "Data File". In the screen that appears, enter your e-mail address in the "To" field, tap "Done" and "Send". In your inbox you should receive a message from trumalabquest@gmail.com that has the LoggerPro data file attached.

   b. You can also transfer the data file to a USB flash drive by inserting the drive into the USB port on the LabQuest and tapping "File" and "Save". The screen that appears should have a USB drive icon on the top left of the screen, if it does not, be sure the USB drive has been inserted completely. Tap on the USB icon to select the flash drive and tap "Save" to save the file to the drive.

8. Either in LoggerPro or by exporting the data to an Excel spreadsheet (see the LoggerPro's "Help" menu for instructions if necessary), graph your data (pH on the Y-axis, volume of titrant on the X-Axis), and determine the end point(s). From the graph, it is possible to determine the acid dissociation constant(s), K_a, or the base dissociation constant(s), K_b. One useful method for doing so employs the Henderson-Hasselbach equation:

$$pH = pK_a - \log([HA]/[A^-])$$

$$\text{or } pOH = pK_b - \log([B]/[HB^+])$$

9. Using three points on your graph, obtain an average K_a or K_b value. If you have not obtained a sufficient number of points near the end point, you may wish to repeat the titration since you now know the approximate location of the end point.

10. Attempt to identify your unknown, justifying your proposed compound. On your unknown cards, please report the following:

    a. Whether you had an acid or a base.

    b. Standard solution used and its molarity.

    c. Size of the 3 samples used for number 6.

    d. Each equivalent weight and the average.

    e. 3 K_a or K_b values and their average.

    f. Your best attempt at the identity of your compound.

APPENDIX 1: Collecting Titration Curve Data using the LoggerPro interface and a computer

Procedure for using *a LoggerPro interface and computer* to determine titration curve. (Portions adapted from the Vernier website)

NOTE: If you are unfamiliar with the LoggerPro system, please read the Introduction to LoggerPro 3 available at chemlab.truman.edu.

A. 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.

B. Start the Logger *Pro* program on your computer. The software should automatically recognize the presence of the LabPro interface and indicate that by showing the LabPro icon immediately below the button bar near the top left corner of the display.

C. Click on the LabPro icon (or select the LabPro by clicking on the Experiment menu and selecting Set Up Sensors).

   1. In the window that opens, ensure that the pH probe and Drop Counter are mapped to their corresponding channels. If they are not, they can be mapped by clicking on the appropriate icon for the sensor and dragging it to the desired channel.

D. Click on the Data Collection icon (the one that looks like a stopwatch) to bring up the data collection window. This window can also be accessed through the Experiment menu.

   1. In the data collection window, click on the Mode drop down list and select **Digital Events**.
   2. Ensure that "By Pressing the Stop Button on the Toolbar" is selected under End Collection
   3. Click Done
   4. You should now have at least one plot on the display that has pH on the y-axis and volume on the x-axis. If more than one such plot appears, it can be deleted.

E. Obtain the plastic 60 mL reagent reservoir. Close both valves by turning the handles to a horizontal position. Follow the steps below to set up the reagent reservoir for the titration.

   1. Rinse the reagent reservoir with a few mL titrant.
   2. Use a utility clamp to attach the reservoir to the ring stand.
   3. Fill the reagent reservoir with slightly more than 60 mL of the titrant (the exact volume isn't critical.
   4. Place a waste beaker beneath the tip of the reservoir and drain a small amount of the titrant into beaker so that it fills the reservoir's tip, then close both valves.

F. Calibrate the drops that will be delivered from the reagent reservoir

1. From the "Experiment" menu in LoggerPro, choose "Calibrate" and select the Drop Counter.
2. Place a 10 mL graduated cylinder directly below the slot on the Drop Counter, lining it up with the tip of the reagent reservoir.
7. Open the bottom valve on the reagent reservoir (vertical). Keep the top valve closed (horizontal).Click the Start button.
8. Slowly open the top valve of the reagent reservoir so that drops are released at a slow rate (~1 drop every second or two). You should see the drops being counted on the computer screen. If you don't see this, consult your instructor.
9. When the volume of the titrant solution in the graduated cylinder is between 9 mL and 10 mL, close the **bottom** valve of the reagent reservoir.
10. Enter the precise volume of titrant solution (read to the nearest 0.1 mL) in the edit box. Also record the number of Drops/mL displayed on the screen in your notebook.

G. Calibrate the pH sensor using two pH buffers (7 and 4 if titrating with base or 7 and 10 if titrating with acid)
   1. From the "Experiment" menu in LoggerPro, select "Calibrate" and choose the pH Sensor.
   2. Immerse the pH Sensor in the pH 7 buffer. Click "Calibrate Now". The value under "Reading 1" should begin to approach 7.00. Once it has stabilized, click "Keep"
   3. Remove the pH sensor from the pH 7 buffer, rinse it with distilled water, and immerse it into the second buffer. The value in "Reading 2" should approach the pH of this buffer. Once it has stabilized, click "Keep"
   4. Click "Done" to exit the calibration routine. The pH sensor is now ready for use. It should be removed from the buffer solution and placed into your unknown solution.

H. Assemble the apparatus
   1. Place the magnetic stirrer on the base of the ring stand.
   2. Insert the pH Sensor through the large hole in the Drop Counter.
   3. Lift up the pH Sensor, and place the beaker containing the unknown solution onto the magnetic stirrer. Lower the pH Sensor into the beaker.
   4. Place a small magnetic stir bar in the solution, making sure that it does not touch the bulb of the pH Sensor. Adjust the position of the Drop Counter as necessary.
   5. Adjust the reagent reservoir so its tip is just above the Drop Counter slot.
   6. Turn on the magnetic stirrer so that the stir bar is stirring at a moderate rate.

I. You are now ready to begin collecting data. Click "Collect". 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 1-2

seconds. When the first drop passes through the Drop Counter slot, check the data table to see that the first data pair was recorded.

J. Continue collecting data until you observe a plateau in the pH. When the reaction is complete, turn the bottom valve of the reagent reservoir to a closed (horizontal) position. Titrate until no appreciable change in pH occurs (about pH 12 if adding NaOH or pH 2 if adding HCl). This should put you well past the end point.

Continue with step 8 on page 4.

APPENDIX 2: ALTERNATE METHOD FOR COLLECTING TITRATION CURVE DATA

Titrate the compound, following the titration with a pH meter. You will need to obtain a pH meter with an electrode and a stir bar. Consult your instructor on the proper use of the pH meter. Weigh out 1 gram (to the nearest 0.1 mg) into an appropriately sized beaker. Dissolve the sample as you found necessary before in 100-150 mL of solvent. If you heat your solution, let it cool to room temperature before titrating. If you wish to use an indicator for this titration, use phenolphthalein for an acidic unknown, methyl red for one that is basic. An indicator is not essential for this titration, since you are monitoring the pH of the solution with the meter. Titrate, recording milliliter and pH readings. It is probably best to add the titrant in ca. 1 mL increments until near the equivalent point when very small increments must be added. Be sure to allow the pH meter to equilibrate before adding the next volume of titrant. Titrate until no appreciable change in pH occurs (about pH 12 if adding NaOH or pH 2 if adding HCl). This should put you well past the end point.