Experiment 10

pK_a AND MOLAR MASS OF A WEAK ACID

Adapted by the Chemistry Faculty of Eastern Michigan University from EQUL 305, written by Richard C. Bell, Lebanon Valley College, published by Chemical Education Resources, Inc.

PURPOSE

Prepare a titration curve for an unknown monoprotic weak acid, and from the titration curve determine the pK_a and the molar mass of the acid.

ACID STRENGTH IS DEFINED BY AN EQUILIBRIUM CONSTANT

Acid strength refers to the tendency for the ionization reaction to proceed to the right. For the acid HA this can be described as

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \quad (1)$$

Acid strength is given quantitatively by the size of an equilibrium constant. Usually the equilibrium constant for Equation 1 is used. This equilibrium constant is called K_a, and is defined by:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad (2)$$

Recall that water's concentration does not appear in the equilibrium constant expression.

HOW CAN K_a BE DETERMINED?

There are three ways you can imagine how K_a could be experimentally determined.

The direct approach would be to measure [H_3O^+], [A^-] and [HA] at equilibrium, plug those numbers into Equation 2, and solve for K_a. Unfortunately, [A^-] and [HA] usually cannot be measured directly.

A second approach would be to prepare a solution containing known amounts of A^- and HA, and measure [H_3O^+] (with a pH meter). Again, plugging those numbers into Equation 2 would allow calculation of K_a. This approach is fine, if we know what the acid is. If the acid is unknown, there is no way to measure out known amounts of A^- and HA.

A third approach, called the titration method, must be used when the acid is unknown, as is the case in this experiment. In our case, we are titrating the weak acid HA with the strong base titrant OH^-, as shown in Equation 3.

$$HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l) \quad (3)$$

Notice that the titration, or neutralization, reaction converts HA to A^-, as the titration proceeds. At any time at or before the equivalence point, the moles of A^- formed will equal the moles of OH^- added. It makes sense then that when half of the HA has been titrated, the concentrations of HA and A^- will be equal. Thus, [A^-] / [HA] = 1 and the [H_3O^+] at that point equals K_a, according to Equation 2.

How can you tell when you have titrated half of an unknown sample? The trick is to titrate the entire sample, and then say that the midpoint of the titration was the point where you had added half the amount of titrant necessary to get to the equivalence point. If you keep track of the solution's pH throughout the titration, you can determine the K_a simply by noting what the pH was at the midpoint.

WHAT IS THIS pK_a BUSINESS?

We have tried to convince you in lecture and in the previous experiment that pH was a convenient way to describe $[H_3O^+]$. For similar reasons, we often simplify the expression of equilibrium constants by referring instead to their negative logarithms, or p*K*'s. For example, pK_a = -log K_a. Values of weak acid pK_a's run from about 1 to 14.

Because pK_a's are commonly used, rather than K_a's, and because pH is more commonly measured, rather than $[H_3O^+]$, the K_a expression is usually used in a form containing pK_a and pH, rather than K_a and $[H_3O^+]$.

This alternative form of the K_a expression can be derived by taking minus the log of both sides of Equation 3, and remembering (from algebra) that the log (*ab*) = log *a* + log *b*. Thus,

$$-\log K_a = -\log\left(\frac{[H_3O^+][A^-]}{[HA]}\right)$$

$$-\log K_a = -\log\left([H_3O^+]\frac{[A^-]}{[HA]}\right)$$

$$-\log K_a = -\log[H_3O^+] - \log\left(\frac{[A^-]}{[HA]}\right) \quad (4)$$

which, upon substituting the symbols for pK_a and pH and rearranging so that pH is on the left, gives us

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad (5)$$

Equation 5 is especially popular with biochemists, who refer to it as the Henderson-Hasselbalch equation. It contains neither more nor less information than the original K_a expression. But, because it directly relates pH and pK_a, it is often perceived as a more convenient form of the equilibrium constant expression—even if it is harder to spell.

Notice how Equation 5 describes the K_a = $[H_3O^+]$ condition at the midpoint of a titration. It tells us that pH = pK_a when $[A^-]$ = [HA], because $[A^-]$ / [HA] = 1 and log 1 = 0. In other words, the pH halfway through a titration equals the pK_a of the acid being titrated.

WHAT IS A TITRATION CURVE?

A titration curve is a graph of the pH of a solution (y axis) as a function of how much titrant has been added (x axis). To make a titration curve, you must measure the pH of the solution being titrated after each of numerous additions of titrant, and you must carefully record the volume of titrant used after each addition. Then, pH is simply plotted against total amount of titrant added.

Titration curves have that characteristic wiggle shape. They are flat at the ends and steep in the middle. This shape basically results from the fact that pH is a log function. Each pH unit corresponds to a factor of ten change in $[H_3O^+]$, and it takes much more acid or base to change the concentration by a factor of ten at the extremes of the pH range. An example titration curve is presented in Figure 1.

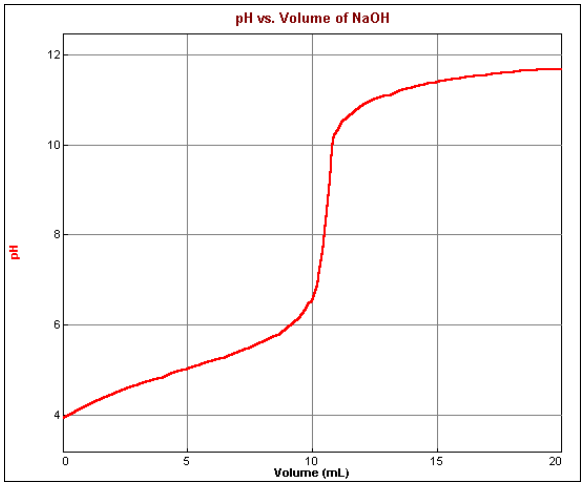

Figure 1. A typical titration curve for a weak acid titrated by a strong base (NaOH).

WHERE IS THE EQUIVALENCE POINT?

The equivalence point, or endpoint, is indicated by the center of the steep part of the titration curve. At this point, the moles of base added equals the moles of acid originally in the sample. So, the "mass of the acid" divided by the "moles of base added" equals the molar mass of the acid.

Locating the center of the steep part of the titration curve can be somewhat arbitrary. Mathematically, the equivalence point is located where the curve is the steepest; that is, it has the largest change in pH per change in volume. This quantity (change in pH divided by change in volume) is the **first derivative**. A graph of the first derivative vs. volume is shown in Figure 2.

Notice in Figure 1 that the equivalence point is around pH 9. If this had been the titration of a strong acid with NaOH, the equivalence point would have been at pH 7. However, because of hydrolysis by the conjugate base formed during the titration of a weak acid, the pH at the equivalence point is slightly basic.

HOW TO SEE BUFFERING AND FIND pK_a

The volume of titrant halfway from the origin to the equivalence point corresponds to the point where half of the acid has been titrated, or converted to its conjugate base. This is the point where $[A^-] = [HA]$, and, according to equation (5), $pH = pK_a$. Thus, the pK_a is easily determined from the titration curve just by noting the pH at the volume halfway to the equivalence point. So, for the acid in Figure 1, pK_a = pH at 5.35 mL (= ½ of 10.7 mL), which is about 5.1.

Notice in Figure 1 that the halfway point is an inflection point (where the curvature changes direction). It is also the point where the titration curve is closest to flat, or, where the pH changes the least when base is added. In other words, this is a buffer solution! You can see that buffering is best at $pH = pK_a$, where there are equal amounts of the acid and conjugate base. So, the titration curve actually shows the buffer phenomenon.

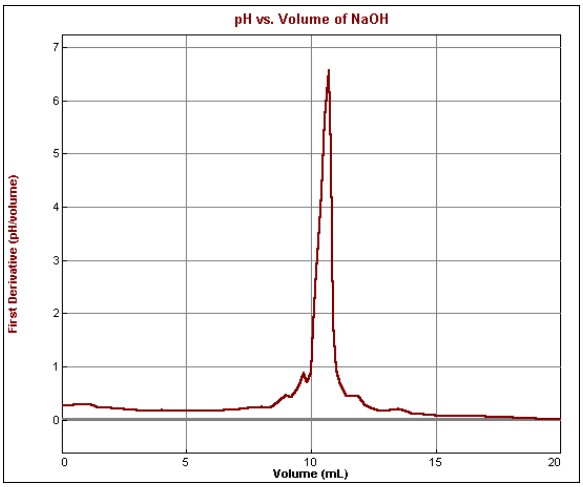

Figure 2. First derivative vs. volume for the titration curve shown in Figure 1 (this graph is mistitled). The largest value of the first derivative is at the volume corresponding to the equivalence point (10.7 mL).

IN THIS EXPERIMENT

You will titrate a sample of an unknown monoprotic acid. A titration curve will be constructed, and from it you will determine the equivalence point volume and the pK_a of the acid. From the moles of base required to reach the equivalence point, and from the mass of your sample titrated, you will determine the molar mass of the unknown acid.

PRE-LABORATORY PREPARATION

1. Read the procedure and data analysis sections of the experiment.

2. Complete the PRELAB assignment in Canvas. Refer to the procedure and data analysis sections of the experiment as needed. The prelab questions for this experiment guide you to determine the appropriate sample size to use and will prepare you to calculate the unknown's molar mass.

3. Construct a complete, organized data sheet. All pH data will be collected by computer and do not need to be recorded on the data sheet. All you need to record are the [NaOH] and the mass of acid used.

EXPERIMENTAL SECTION

REAGENTS PROVIDED

NaOH(aq), approximately 0.05 *M*.
Unknown acid.

Hazardous Chemicals

Handle the acid and base solutions with care.

WASTE DISPOSAL

All of the chemicals used in this experiment may be safely disposed of by washing down the sink.

PROCEDURE

Unless told otherwise, you will do this experiment with a partner (or two, if necessary).

SET UP FOR DATA COLLECTION

1. Setup and do a two-buffer calibration of your pH electrode following the directions in the Techniques section (located after the procedure section).

In this experiment we are primarily measuring the pH of acidic solutions, so we will use pH 4 and 7 buffers to calibrate the pH electrodes.

2. Set up the LabQuest2 to collect data for a titration curve. To do this:

a. Tap on the **Mode box** (on the right side of the screen)
b. Select ***Events with Entry*** from the top scroll box.
c. Enter *Volume* as the name and *mL* as the units. Tap ***OK***.

SAMPLE PREPARATION

3. Clean a 50 mL buret, and load it with standardized NaOH (approximately 0.05 *M*). Position the meniscus exactly on 0.00 mL.

Record the actual NaOH concentration on your Data Sheet.

4. Weigh out a sample of your unknown acid on weighing paper and transfer it into a 250 mL beaker (see prelab calculations).

Record the unknown number and the measured mass on your Data Sheet.

5. Add about 75 mL of distilled water to dissolve the unknown acid.

PERFORM THE TITRATION

6. Immerse the pH electrode in the unknown solution. Position the buret over the beaker.

7. Tap the *Start* button.

8. Wait until the pH reading stabilizes, then tap *Keep*. Type the initial buret reading (0.00) into the box that appears and tap *OK*.

9. Titrate the acid. To do this:

a. Add about 1 mL of NaOH from the buret. Add less than 1 mL when the pH is increasing rapidly. The pH should increase by no more than 0.2 after each addition of base. See the discussion below for more information.)
b. Stir the solution.
c. Tap ***Keep*** when the pH reading stabilizes.
d. Enter the buret reading (to the nearest 0.01 mL) into the box and tap ***OK***.
e. Repeat steps a-d until the curve is complete.

Remember: a buret tells you the volume delivered, not the volume actually in the buret. So, just record the volume delivered – you do not need to subtract from 50.

The more readings you take, the nicer curve you will get. The readings do not have to be equally spaced. It makes sense to add larger increments of titrant (up to 1 mL) when the pH is changing slowly, and very small increments when the pH is changing rapidly. In fact, you should go one-drop-at-a-time near the equivalence point.

You may want to rescale the graph axes as necessary to get a good view of your graph. To do so, tap ***Graph*** (in the top menu) then ***Autoscale Once***.

Take readings until you are well past the equivalence point (by at least 8 mL), into the region where the pH is changing slowly again (the last flat part of the curve in Figure 1). If you do not take these readings it may be difficult to precisely locate the equivalence point!

If you enter the wrong volume or hit the keep button at the wrong time, the volumes that you enter can be edited after you tap **Stop**. Tap on the Data Table icon, double-tap on the cell in the data table, enter the correct value, and tap ***Done***.

If there is a measured pH value to be deleted, this can also be done after you have finished collecting all of your data and you have hit the **Stop** button. To delete a point, tap on the row in the data table, then tap ***Table,*** then *tap* ***Strike Through Data***. (This process can be reversed by following the same procedure, but choosing ***Restore Data*** as the last step.) So you don't need to panic or start over.

If you accidentally hit the Stop button too soon, you can resume by tapping on the **Start** button and then choosing ***Append***.

10. Tap on the Stop button when you are finished collecting data.

11. Decide whether to repeat the titration.

If you are satisfied with your first titration and you have sufficient data and did not miss the equivalence point, proceed to the next step.

Otherwise, repeat the titration taking advantage of what you've learned from the first titration. Note the regions where the pH changes slowly and rapidly.

12. Print out a copy of your titration curve.

a. Tap on the **Graph icon** (if you are not on the Graph screen).
b. Tap ***File*** from the top menu.
c. Tap ***Print*** and then ***Graph***.
d. Tap on ***Print Graph Title***.
e. Enter an appropriate graph title.
f. Tap ***Print***.

DATA ANALYSIS

13. To aid in determining the location of the equivalence point, we will construct a first derivative graph (see figure 2). To do this:

a. Tap the **Data Table** icon. Then tap ***Table***, and then ***New Calculated Column***.
b. Enter *FD* for the Name and *pH/mL* for Units.
c. For the Equation Type, choose *1st Derivative(Y,X)* from the scroll box (it is near the bottom). By default, the Column for X should be *volume* and the Column for Y should be *pH*, which are what is desired.
d. Tap ***OK***. The graph should now re-appear with the first derivative on the y-axis.

   The peak in the first derivative graph should be at the same volume as the steep rise in the titration curve. If not, something is wrong.
e. Print this graph (see step 12 for directions).

14. Print out the complete Data Table.

Tap ***File***, then ***Print***, then ***Table***, then ***Print***.

15. Rinse the pH electrode, wipe it with a Kimwipe and return it to its storage bottle. Dump leftover solutions down the drain. Rinse, dry, and store your glassware.

16. Shutdown the LabQuest2.

Tap ***File****, then* ***Quit***. Choose to ***Discard*** the data. Next, tap on the ***System*** folder and then ***Shut Down*** and, finally, ***OK***.

RETURN EVERYTHING TO WHERE IT WAS AT THE START OF LAB. HAVE AN INSTRUCTOR CHECK YOUR STATION BEFORE LEAVING.

Once your station is clean, wash your hands.

TECHNIQUES

CALIBRATION AND USE OF A pH PROBE

1. Turn on the LabQuest2 by pressing the red power button on the top.

It takes a minute to warm up.

2. Once warmup is complete, connect the pH Probe amplifier box to CH 1 on the left end of the LabQuest2.

Most of the pH probes will immediately be recognized and a box will appear containing the pH reading.

If the meter box does not appear, you have an older probe with an analog-to-digital adapter and it needs to be set up manually, as follows:

a. Tap ***Sensors*** from the top menu line.
b. Tap ***Sensor Setup…*** .
c. Tap in the large box next to CH 1 that reads "No Sensor".
d. Scroll down and tap ***pH/mV/ORP Amplifiers***.
e. Tap on ***pH***.
f. Tap ***OK***.
g. Tap ***OK*** to return to the meter screen, where you should now see the pH reading.

3. Prepare the electrode for use.

Remove the electrode from its small plastic storage bottle by unscrewing the top until you can slide the electrode out of the bottle. Set the bottle aside where it will not get knocked over. Rinse it off thoroughly (see the RINSING A pH ELECTRODE section, below).

4. Calibrate the pH electrode.

a. Tap on ***Sensors*** from the menu line at the top of the screen. Next choose ***Calibrate*** and then ***CH1: pH***.
b. Tap ***Calibrate Now***.
c. Immerse the electrode in a bottle containing a pH 4 or 7 buffer and swirl it for a few seconds to remove any air bubbles or dilute any water droplets clinging to the end of the electrode. The bulb at the bottom of the electrode must be completely submerged in order to get an accurate reading.
d. In the Value 1 box, enter the buffer pH (4 or 7).
e. Wait until the line voltage reading stabilizes and then tap ***Keep***. Frequently, the last digit will be fluctuating—this is normal.
f. Remove the electrode from the solution and rinse it thoroughly.
g. Place the electrode in the other buffer solution and swirl it briefly (a few seconds).
h. In the Known Value 2 box, enter the buffer pH (4 or 7).
i. Wait until the line voltage reading stabilizes and then tap **Keep**. The voltage should have changed by approximately 0.6 – 0.8 V.
j. Tap **OK**.

If the calibration was done properly, the pH reading on the screen should be roughly equal to the pH of the last buffer solution ($\pm$ 0.03).

You are now ready to measure the pH of solutions. Simply immerse the pH electrode in a solution, swirl briefly to equilibrate, and read the pH when it stabilizes.

RINSING A pH ELECTRODE

1. Thoroughly rinse the electrode by spraying it with distilled water from a wash bottle. Be sure to spray the bottom where the sensitive pH glass is located.

2. Wipe the outside with a Kimwipe, and then give it a couple of firm shakes to remove the water from the bulb. Do NOT dry the bulb of the electrode with a Kimwipe or a paper towel.

The glass bulb of the pH electrode is very fragile. Be careful not to drop the electrode or hit it against something (like the edge of the sink or your lab partner), electrodes are expensive (and lab partners are valuable)!

Name _____ Station Used _____ Instructor/Day/Time _____

Partner _____ Station Checked & Approved _____

DATA SHEET & DATA ANALYSIS

Record any observations, concentrations, masses, or other useful data gathered during the experiment.

1. Determine the volume at the equivalence point from looking at your two graphs. Since, it is not easy to read the graphs precisely, use your printed data table to more accurately determine the equivalence-point volume.

equivalence-point volume _____

2. Determine pK_a from your titration curve. To do this, on your printed titration curve:

a. mark and label the equivalence point on the titration curve;
b. mark the midpoint volume on the x-axis (point at one-half the volume used to get to the equivalence point);
c. draw a vertical line from the point marked in (b) to the titration curve; and
d. draw a horizontal line from the marked point on the titration curve (in part (c)) to the y-axis.

Again, use your data table to confirm your value (interpolating or averaging as necessary). Report your midpoint volume and pK_a to the number of significant figures of which you are confident.

midpoint volume _____ pK_a _____

3. Calculate the molar mass of your unknown acid.

Molar Mass of Unknown Acid_____

Unknown Number_____

"The lab has ended. Depart in peace."