EXPERIMENT 4

Determination of Acid Constant, K_a, using a buret

PURPOSE:
The purpose of this experiment is to determine the K_a of an acid from its molar concentration and from its titration curve.

INTRODUCTION:
When an acid is dissolved in water, it reacts with the water according to the equation:

$$HA(aq) + H_2O(1) \rightarrow H_3O^+(aq) + A^-(aq) \qquad \textbf{(1)}$$

The reaction is reversible and so establishes an equilibrium with a constant, K_a, based on the relationship:

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

From this the familiar Henderson-Hasselbalch Equation is derived:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad \textbf{(3)}$$

During the course of a titration, an acid in solution reacts with a base in solution.

$$HA(aq) + OH^- (aq) \rightarrow A^- (aq) + H_2O (1) \qquad \textbf{(4)}$$

At the equivalence point the titration is complete, no HA remains; all is in the form of the conjugate base, A^-, and water. Halfway to the end point, half of the HA has reacted to become its conjugate base A^- and water. At that point, the concentrations of HA and A^- are equal. When these concentrations are equal, log $[A^-]/[HA]$ is zero and $pH = pK_a$ (Equations 3). It is clear then that pK_a can be read directly from the titration curve as the pH at the half-way point of a titration.

There are several parts to this experiment. The general plan is to:

1. Prepare and standardize a base solution for titrating the acid solution,
2. Determine the molarity and pH of the acid solution with the standardized NaOH and use the equilibrium expression to calculate K_a,
3. Titrate the acid with the base to develop the titration curve, and interpret the curve to determine the molarity of the acid solution and the K_a of the acid.
4. Perform a half-titration of acetic acid with sodium hydroxide to determine the K_a.

Part I: Preparation and Standardization of the NaOH Solution

It will be necessary to prepare 500 mL of an approximately 0.1 M NaOH by diluting a the appropriate amount of 6.0 M NaOH(aq) to about 500 mL.

Shelf reagents are not prepared to any high degree of accuracy, and even if they were, could not be kept long at a particular concentration due to gradual changes from exposure. If a solution is prepared from a shelf reagent by dilution, no matter how carefully measurements are made, the result will be a solution of undetermined concentration. It must be standardized to know its concentration beyond two significant figures.

Potassium hydrogen phthalate, ($KHC_8H_4O_4$), abbreviated KHP, is a monoprotic weak acid that is commonly used as the primary standard. It reacts with sodium hydroxide according to

$$KHC_8H_4O_{4(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(l)} + Na\,KC_8H_4O_{4(aq)} \qquad \textbf{(5)}$$

Titration with of a known mass of KHP to the endpoint with a carefully measured volume of NaOH is performed. Equation (5) allows one to determine the number of moles of NaOH needed to reach the endpoint. Given the volume of NaOH dispensed to reach the endpoint one can then calculate the molarity of the NaOH.

1. Measure out about 0.5 gram of KHP on an analytical balance and record the weight to four significant figures. Use the weighing bottle technique to measure out the KHP by first weighing a shell vial of KHP, dispensing some KHP into a dry 125 mL Erlenmeyer flask and then reweighing the vial of KHP. Repeat this process until the mass of KHP in the vial is reduced by about 0.5 g. When this is the case this means you have transferred about 0.5 g of KHP to your Erlenmeyer flask.

2. Dissolve the KHP in approximately 50mL of deionized water. Add 2-3 drops of phenolphthalein indicator and titrate the KHP solution with the NaOH solution from a buret to a light pink color. Determine very precisely the volume of base required to reach the endpoint by approximating between the marks on the burette for a fourth significant figure.

3. Repeat the titrations until you have three reliable trials. A proper standardization requires a minimum of three trials that agree within plus or minus 0.5% of each other. A quick check of the reproducibility of your titrations is to calculate the ratio of g KHP/mL NaOH to four significant figures. This ratio should vary only in the last significant figure. Repeat the standardization process until three trials do agree within these limits. Calculate the molar concentration of the base from the data from each trial and then calculate the average concentration.

Part II: Determine the Molarity and pH of the Acetic Acid Solution

Acetic acid is a monoprotic weak acid and will be neutralized by sodium hydroxide according to

$$CH_3COOH(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCH_3COO(aq) \qquad \textbf{(6)}$$

You will use your standardized sodium hydroxide to determine the molarity of the acetic acid solution.

1. Obtain about 150 mL of the acetic acid solution of unknown molarity from your instructor. Transfer a small portion of the acetic acid unknown to a small (10 mL or 30 mL) beaker.

2. Perform a two-point calibration of your pH meter with pH 4 and pH 7 buffer. Once the pH meter is calibrated, measure the pH of your acetic acid solution and determine the $[H_3O^+]$.

3. Use a volumetric pipette to transfer a 25.00-mL sample of the acetic acid solution to a 125-mL Erlenmeyer flask. Add 2-3 drops of phenolphthalein indicator to the sample.

4. Fill your buret with your standardized sodium hydroxide solution and titrate to the endpoint. Repeat until you obtain three reproducible trials. Report the average molarity of the acetic acid solution to <u>four significant figures</u>. Use this molarity and the pH from step 1 to calculate K_a from equation (2) above.

Part III: Develop a Titration Curve to Determine the Molarity and K_a

BURET DIRECTIONS: SEE INSTRUCTOR FOR SET-UP.

<u>A. Data Collection</u>

NOTE: This will be performed in place of the existing procedure for developing a titration curve. The Vernier LabQuest with pH probe and buret will be used. Collect from the Stockroom: 1-pH sensor for the Venier, a buret, Vernier LabQuest computer, & a stir bar.

1. Connect the pH sensor to Channel 1 on the LabQuest. Choose **New** from the File menu.

2. Perform a two-point calibration of the pH electrode with pH = 4 and pH = 7 buffers. To calibrate the pH sensor: Either tap on ***SENSORS*** menu at the top of the screen choose ***CALIBRATE*** then **CH1: pH** or tap on the numerical value associated with pH on the center screen and a pop-up for ***CALIBRATE*** will appear. The next screen should exhibit a tab labeled ***CALIBRATE NOW*** located top left of the screen, place the sensor in the buffer 7 solution, allow the numerical values on the top right to stabilize then press ***KEEP***. Clean the electrode in deionized water and place the electrode in the buffer 4. Once again stabilize and press ***KEEP***. The pH sensor is now calibrated.

3. Set up the buret, clean it with soap and water and fill it with 10 mL of your standardized NaOH(aq) solution. Flush out any air bubbles in the tip by draining the NaOH(aq) solution into a waste beaker. Rinse the inside of the buret with your NaOH solution.

4. Refill your buret with the NaOH solution. With a volumetric pipet transfer 25.00 mL of your acetic acid solution to a 400-mL beaker. Place a magnetic stir bar in your beaker containing your acetic acid solution and place the beaker on the magnetic stirrer on the base of the ring stand.

5. Clamp the pH sensor to the ring stand so it is suspended, on one side, in the beaker containing your acid.

6. Adjust the positions of the buret so it lines up near the center of the magnetic stirrer. Lower the pH sensor assembly into the beaker. Make sure the height is adjusted such that the stir bar does not hit the bottom of the pH electrode. If the level of solution is not high enough to cover the bottom of the pH sensor, add more deionized water to the beaker. Turn on the magnetic stirrer so that the stir bar is stirring at a moderate rate.

7. You are now ready to perform the titration.

i) On the ***Meter*** screen, tap ***Mode***. Change the data-collection mode to ***Events with Entry***. Enter the Name (Volume) and Units (mL). Select ***OK***.

ii) Conduct the titration carefully, as described below.

a. Start data collection on venier (press the green icon)

b. Before you have added any NaOH solution, tap ***Keep***. Enter **0**, the volume in mL and select ***OK*** to save this data pair.

c. Slowly add NaOH to the beaker, swirling, until the pH value changes by a 0.5 increment, tap ***Keep***. Enter the volume, as read from the buret, and then select ***OK***.

d. Continue this process using 0.5 pH increments, each time entering the buret reading, until about pH 10 is reached.

e. Once you have passed the equivalence point, you may use 1.0 mL increments until the pH reaches about 12 or 40 mL of NaOH solution have been added, whichever comes first.

8. ***Stop*** data collection to view a graph of pH vs. volume.

9. Examine the data on the displayed graph to find the equivalence point; to examine the data pairs on the displayed graph, select any data point. Record the NaOH volume, at the equivalence point in your data table.

10. **Save your data to your flash drive!**

11. Dispose of the reaction mixture as directed. Rinse the pH sensor with deionized water in preparation for the second titration.

12. Repeat the titration with a second sample of acetic acid. Analyze the titration results in a manner similar to your first trial and record the equivalence point in your notebook. Use your determination of the equivalence point volume in to calculate the

molar concentration of your acetic acid solution and determine the acid dissociation constant for acetic acid. Print copies of your titration curves to include with your report.

B. Analysis of Titration Curves:

Examine your titration data to identify the region where the pH made the greatest increase. The equivalence point is in this region.

a. To examine the data pairs on the displayed graph, select any data point.
b. As you move the "examine" line, the pH and volume values of each data point are displayed to the right of the graph.
c. Identify the equivalence point as precisely as possible and record this information in your notebook.
d. Store the data from the first run by tapping the File Cabinet icon.

An alternate way of determining the precise equivalence point of the titration is to take the first and second derivatives of the pH-volume data:

Determine the peak value on the first derivative *vs.* volume plot.

a. Tap the Table tab and choose New Calculated Column from the Table menu.
b. Enter d1 as the Calculated Column Name. Select the equation 1st Derivative (Y,X). Use Volume as the Column for X and pH as the Column for Y. Select OK.
c. On the displayed plot of d1 *vs.* volume, examine the graph to determine the volume at the peak value of the first derivative.

Determine the zero value on the second derivative *vs.* volume plot.

d. Tap Table and choose New Calculated Column from the Table menu.
e. Enter d2 as the Calculated Column Name. Select the equation 2nd Derivative (Y,X). Use Volume as the Column for X and pH as the Column for Y. Select OK.
f. On the displayed plot of d2 *vs.* volume, examine the graph to determine the volume when the 2nd derivative equals approximately zero.

Part IV: Perform a Half-Titration to determine the Ka of Acetic Acid (Optional)

In this procedure you first titrate 25.00 mL of 1.00 M acetic acid to the endpoint with 1.00 M sodium hydroxide. You will then back-titrate with the acetic acid until the solution is just slightly acidic, i.e. to just before the endpoint. You then carefully add just enough sodium hydroxide to reach the endpoint again. This will be monitored concurrently with phenolphthalein indicator and the pH meter. Once you have successfully determined the endpoint, you will then add another 25.00 mL of the 1.00 M acetic acid. This will effectively create a half-titrated solution, and the pH will be the pH at the half-equivalence point. This is the pK_a of the acetic acid.

1. Use a 25-mL volumetric pipet to transfer precisely 25.00 mL of 1.00 acetic acid solution to a 250 mL beaker. Add 2 drops of phenolphthalein indicator.

2. Connect the pH electrode to LabQuest and choose New from the File menu. Perform a two-point calibration of the pH electrode with pH = 4 and pH = 7 buffers. Follow the calibration instructions included with the electrode.

3. Fill a 50-mL buret with 1.00 M NaOH solution.

4. Begin the half-titration.
    a. Place the beaker of acetic acid on a magnetic stirrer and add a stirring bar.
    b. Set up a ring stand and clamp to hold the pH Sensor in place. Position the pH Sensor in the beaker so that the tip of the probe is completely immersed.
    c. Turn on the magnetic stirrer and adjust the stirring rate to give *gentle stirring*.
    d. Monitor the pH of the reaction mixture on LabQuest. (Do not tap Start!)
    e. Use your buret to slowly add your NaOH solution, in ~1 mL increments, to the beaker of acetic acid solution.

5. Conduct the titration carefully. As the reaction approaches the equivalence point, at about pH 6, add the NaOH solution drop by drop. Periodically rinse the sides of the beaker with deionized water. When you reach the equivalence point, the pH will increase rapidly and the indicator will change color. If necessary add another drop of NaOH so that the reaction is slightly past the equivalence point. Remember that the pH will not increase rapidly beyond the equivalence point (pH ~10).

6. Now you will check the equivalence point. First, carefully add acetic acid to the solution until the pH is just acidic. Then, carefully add NaOH dropwise to the beaker of reaction mixture, until you reach the equivalence point as precisely as possible. A very slight pink color of the phenolphthalein indicator is visible. At this point you have effectively titrated 25.00 mL of the 1.00 M acetic acid to the equivalence point.

7. Transfer another 25.00 mL of 1.00 M acetic acid from to the 250 mL beaker of reaction mixture. Continue to stir the solution in the beaker thoroughly. By adding the additional 25.00 mL of acetic acid solution you have effectively titrated 50.00 mL total of 1.00 M acetic acid solution to the <u>half-equivalence point</u>. Read and record the pH of the solution in the beaker.

8. When you have finished the testing, dispose of the reaction mixture as directed. Rinse the pH Sensor with distilled water in preparation for a second trial. If time permits, repeat the half-titration with a second sample of the 1.00 M acetic acid solution.

REPORT GUIDELINES/INSTRUCTIONS

Table 1 – Data and Calculation for Standardization
On a separate sheet of paper prepare a table which presents your data for the standardization of the 0.1 M NaOH solution by titration of KHP. Be sure to include all relevant data from each trial, the molarity of NaOH determined from the data from each trial, and the average molarity of the NaOH solution. Provide sample calculations on a separate sheet of paper.

Table 2 – Titration Data (Part II) for Acetic Acid/K_a from Equilibrium Expression
On a separate sheet of paper, prepare a table which presents your data for the titration of the acetic acid solution with your standard sodium hydroxide solution. Be sure to include the average molarity of the acetic acid solution. Also include the pH of the acetic acid solution before you started the titration. Calculate K_a from the equilibrium expression, equation (2). Provide sample calculations on a separate sheet of paper.

Table 3 – Titration Data from Part III (Titration Curves)
Prepare a table that presents your data for the titration of the acetic acid solution from you titration curves. This should include the equivalent point volume, half-equivalent point volume, molarity and average molarity of the acetic acid solution, and the pK_a and K_a of acetic acid. Provide sample calculations on a separate sheet of paper.

Table 4 – Half-Titration Data from Part IV
Prepare a brief table that presents the pKa and Ka results from your half-titration trials. Provide any sample calculations on a separate sheet of paper.

Graphs – Titration Curve
Use LoggerPro to analyze and print your titration curves. Use the titration curve to determine the equivalence point volume, pK_a and K_a for acetic acid; illustrate this on your graph. Print a titration curve graph for each trial performed, if more than one was completed.

Comparison of the acetic acid solution molarities and Ka's – Brief Discussion
Compare the K_a values determined by the different methods employed in this experiment. How closely do they agree with each other? How closely do they agree with the literature value of K_a at 25°C? Also compare the molarities of your acetic acid solution determined by titrating to the endpoint in Part II and by developing titration curves in Part III. How closely do the molarities compare? Discuss possible reasons for discrepancies, and suggest possible improvements to the experimental procedure to improve the result