Experiment

K_{a1} OF PHOSPHORIC ACID BY TITRATION

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LEARNING OBJECTIVES:

The objectives of this experiment are to . . .

- experience the titration of a triprotic acid.
- learn proper technique in pipette and buret usage.
- determine the first dissociation constant for phosphoric acid from the titration curve.
- become familiar with Pauling's rules for oxyacid strength.

INTRODUCTION:

Phosphoric acid, H_3PO_4, has three ionizable hydrogen atoms and is a *triprotic* acid. It ionizes in three steps, each step having a distinctive ionization constant expression and numerical value as:

$$H_3PO_4 + H_2O \Rightarrow H_3O^+ + H_2PO_4^- \qquad K_{a1} = [H_3O^+][H_2PO_4^-] / [H_3PO_4] \qquad (1)$$

$$H_2PO_4^- + H_2O \Rightarrow H_3O^+ + HPO_4^{2-} \qquad K_{a2} = [H_3O^+][HPO_4^{2-}] / [H_2PO_4^-] \qquad (2)$$

$$HPO_4^{2-} + H_2O \Rightarrow H_3O^+ + PO_4^{3-} \qquad K_{a3} = [H_3O^+][PO_4^{3-}] / [HPO_4^{2-}] \qquad (3)$$

Phosphoric acid is a weak acid in its first ionization step and is about 10^{-5} weaker acid in the second and very weak in the third ionization, again by about 10^{-5}. Ionization is fairly complete in the first step, however, we still have some H_3PO_4 molecules in solution. The concentration of the H_3O^+, contributed by this ionization is enough to make the solution significantly acidic. The second dissociation constant of H_3PO_4 is quite small and there is little H_3O^+ from the second ionization step. Therefore, when we observe the titration curve of phosphoric acid, we distinguish two prominent equivalence point regions.

It is necessary for two equivalence points to differ by at least three orders of magnitude to be able to differentiate them. Since the equivalence points for H_3PO_4 differ be about 10^{-5}, the first two equivalence points are readily determined. The third equivalence point is so small it is unobservable in aqueous titrations.

Let us analyze what happens during a titration of 25.00 ml of 0.100 M H_3PO_4 with 0.100 M NaOH. After 12.50 ml of NaOH have been added, one-half of the H_3PO_4 has been neutralized to produce $H_2PO_4^-$, i.e., $[H_2PO_4^-] = [H_3PO_4]$. If we now look at the equilibrium constant expression for the first ionization, i.e.,

$$K_{a1} = [H_3O^+][H_2PO_4^-] / [H_3PO_4] \qquad (4)$$

we can rearrange this to a more convenient form by taking the negative logarithm of both sides to obtain

$$-\log K_{a1} = -\log[H_3O^+] - \log\{[H_2PO_4^-] / [H_3PO_4]\} \quad (5)$$

substituting the "p" function for "-log" gives us

$$pK_{a1} = pH \quad -\log\{[H_2PO_4^-] / [H_3PO_4]\}. \quad (6)$$

This is a rearrangement of a very useful equation known as the Henderson-Hasselbalch equation, as

$$pH = pK_{a1} + \log\{[H_2PO_4^-] / [H_3PO_4]\} \quad (7)$$

As above, at exactly one-half the equivalence point volume, $[H_2PO_4^-] = [H_3PO_4]$, the log term goes to zero, and the pH = pK_{a1}. Thus, the first ionization constant, K_{a1}, can easily be determined from the half equivalence point volume corresponding to the first ionization reaction. This is due to the fact that in the titration of a weak acid with a strong base, a buffer system is formed after the first few ml of base have been added consisting of the weak acid and the conjugate salt of that weak acid as indicated in expression (7), where the pH is controlled around the pK_{a1} by the ratio of $[H_2PO_4^-] / [H_3PO_4]$

When the titration has proceeded half way to the equivalence point, then the concentration of the weak acid is equal to the concentration of its conjugate base as shown, and the pH can then be determined as above and the pH at that volume will then represent the pK_a of the weak acid.

SLOPE AND DERIVATIVES:

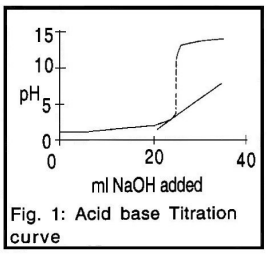

Fig. 1: Acid base Titration curve

A straight line that is drawn in such a fashion that it just touches a curved line at some point is said to be tangent to the curve, as shown in Figure 1. The slope of such a line is given as $\Delta\mathbf{Y}/\Delta\mathbf{X}$, where Δ (delta) is the change of a variable. The slope is also referred to as rise over run. When such a curve is digitized, giving a table of X and Y values, such as are obtained in the MicroLab collection of titration data, then the successive differences of the Y values, divided by the successive differences of the X values, will approximate the slope of each segment of the titration curve. This process is termed "taking the derivative," and is accomplished in an **EXCEL** spreadsheet column by typing in the formula **=(Y2-Y1)/(X2-X1)** where **Y1** is the firstY values cell, **Y2** the second **Y** values cell, and the same for the **X** value cells. This reduces to $\Delta\mathbf{Y}/\Delta\mathbf{X}$ and is termed the "first derivative." This process is repeated for successive pairs of **X** and **Y** values. If one then takes the $\Delta(\Delta\mathbf{Y}/\Delta\mathbf{X})/\Delta\mathbf{X}$, this is termed the "second derivative." This is accomplished in the same manner, using the first derivative as the Y array.

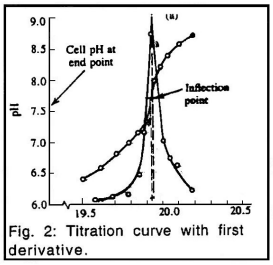

Fig. 2: Titration curve with first derivative.

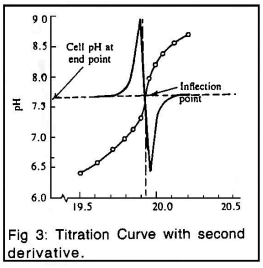

Fig 3: Titration Curve with second derivative.

In the first part of the curve in Fig. 1, the curvature is up to the left, where as in the second part of the curve, the curvature is up to the right. This means that in an ideal curve, the tangent to the curve is increasing in slope to infinity for the first part, and then decreasing in slope from infinity for the second part. Thus, at the equivalence point, the first derivative is theoretically infinite, but in practice will just be very large. The second derivative is the "slope of the

slope," and thus at the equivalence point will be zero. Thus, the first and second derivatives on the pH vs. volume data allows an even more accurate determination of the equivalence point than can be obtained with indicator "end points."

PAULING'S RULES:

Linus Pauling, a Nobel Laureate in chemistry, proposed some simple rules for determining the strengths of oxyacids such as [H_3PO_4]. Ternary acid strengths (K_a's) may vary from greater than 10^8 to 10^{-13}. If one rewrites the formula in the form of $EO_m(OH)_n$, (e.g., for H_3PO_4 this becomes $PO_1(OH)_3$ and m = 1, n = 3) and then examines the relationship of acid strength (K_a) to the value of "m," an interesting correlation emerges:

m	K_a	Strength	Example	
3	~ 10^8	Very strong	$HClO_4$	$ClO_3(OH)$
2	~ 10^3	Strong	$HClO_3$	$ClO_2(OH)$
1	~ $10^{-2, -4}$	Weak	$HClO_2$	$ClO_1(OH)$
0	~ $10^{-7, -9}$	Very weak	HClO	$ClO_0(OH)$

In the above Ka values, the actual values may vary by several orders of magnitude, i.e., 10^{-2} to 10^{-4}, and the range between K_a's may be from 10^{-3} to 10^{-6}.

Multiple hydroxyacid equilibrium constants (K_a's) will usually differ by about 10^{-5}, e.g., for H_3PO_4, $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, and $K_{a3} = 4.2 \times 10^{-13}$. These general rules are very helpful in estimating ternary acid strengths.

INSTRUMENTATION:

pH can be very precisely measured by the use of an electronic instrument called a pH meter, which consists of a sensor, called the pH probe, associated electronics to modify the signal for proper display, and the readout device for displaying the values to the operator. In order for the information on the display to be meaningful, the system must be calibrated to solutions of known pH. Since there are several equivalence points in the titration of H_3PO_4, calibrating the pH probe over the range from 4, 7, and 10 will provide an adequate range. The pH probe, ***MicroLAB*** interface, computer and associated software will serve as the associated electronics and readout device of the pH meter.

CAUTIONS OF CHEMICAL HAZARDS:

H_3PO_4 solution: Severely corrosive to eyes, skin and other tissue. Toxic, strong skin irritant.

NaOH solution: Corrosive liquid, skin burns are possible, very dangerous to eyes.

The other chemicals are innocuous, however you should keep all chemicals away from eyes and mouth, wash hands after use and before leaving the laboratory, and use prudent laboratory practices at all times.

EQUIPMENT:

You will need to have the following equipment available per pair of students before beginning this experiment.

1 - Dropping buret system
1 - 5 ml pipet
1 - 10 ml beaker
1 - utility clamp
1 - pipetting bulb
4 - 250 ml beakers

1 - magnetic stirrer with stirring bar
1 *MicroLAB* drop counter
1 - pH probe with a BNC connector
1 - ring stand
1 - clamp for the counter
1 - *MicroLAB* interface and two *MicroLAB*. programs (***Drop Counter Calibration*** and one of the titration experiments, as per your instructor) to do the titration.

CHEMICALS:

The following chemicals will be provided for you in the laboratory. Please take no more than the recommended amounts.

100 ml of 0.100 M NaOH solution
30 ml of 0.100 M H_3PO_4 solution
15 ml each of pH 4, 7 and 10 buffer solutions per pair of students in 25 ml beakers.

PROCEDURE:

1. Fill the dropping buret just above the top mark with the 0.100 M NaOH.

2. Pipet exactly 5.00 ml of the 0.100 M H_3PO_4 solution into each of four 250 ml beakers and add 35 ml of distilled water. (Your instructor will provide you with the details on proper pipetting techniques.)

3. Connect your pH probe to the pH - BNC connector, press the "Power ON" button, open the ***MicroLAB*** software and Click on **pH** in the **Variables View** and recalibrate your probe with the pH 4, 7 and 10 buffers supplied. Be sure to rinse the pH probe with distilled water after each buffer and before you place it in your analyte solution. Between titrations, the probe should be stored in the pH 7 buffer, then rinsed well with distilled water before inserting into your titration beaker. **CAREFULLY** (the glass bulb is **very** fragile) shake any excess water off, and again after the calibration and before you place it in your analyte solution. If you are unfamiliar with this procedure, look it up in **The Measurement Manual.** **PLEASE BE VERY CAREFUL NOT TO HIT THE EDGE OF THE CONTAINERS WITH THE TIP OF THE pH PROBE. IT IS VERY FRAGILE AND EASILY BROKEN. THEY COST ABOUT $90 EACH.**

4. Open the ***MicroLAB*** program ***Drop Counter Calibration*** and calibrate the dropping buret according to the instructions from your instructor. This calibration should be repeated after completing the titrations and the values averaged.

5. Open the instructor indicated ***MicroLAB*** program to carry out the four titrations as indicated in the directions for dropping buret titrations. Between titrations, the probe should be stored in the calibration buffer, then rinsed well with distilled water before inserting into your titration beaker.

6. When you are ready to begin taking data, click on **Start**. The program will not take any data until the first drop passes through the drop counter. Thereafter, the titration will be automatic.

7. Continue the titration until the titration curve has begun to flatten out at the top.

8. After you have collected your first titration data, click Stop, **Repeat Experiment**, **Save** the data as a file with a meaningful name such as **H_3PO4Titr1.DH**. The application will then be ready to take the next set of titration data.

9. Repeat the above process for each of the 5.00 ml samples of phosphoric acid.

10. **CAUTION:** Be sure to use and record in your lab notes and on your report sheet a different file name for each of the titrations so you can recover them for printing and calculating later.

DATA ANALYSIS

1. For each of the data files, do the following:
   a. Using **Analysis**, calculate the first derivative of pH vs. volume and click-drag it to column C, and the second derivative and click-drag it to column D

   b. Print out two graphs for each titration as follows:
      i. Graph 1: Titration curve on Y1 with first derivative on Y2
      ii. Graph 2: Titration curve on Y1 with second derivative on Y2

   c. Show all of the following calculations in your lab notes for each of the titrations, but also show them in your report. Using the second derivative, calculate, by interpolation (see the appendix for details on how to do this), the exact volume needed to the first equivalence point for each of the titrations

   d. Calculate the number of mmols of NaOH used for each titration from the milliliters used and the given concentration of the standard and enter the values on the report sheet.

   e. Calculate the volume to ½ of the first equivalence point volume from this value as indicated in the introduction.

   f. Locate the region of the data table containing this calculated volume.

   g. Calculate by interpolation the exact pH corresponding to this half equivalence volume. This will be the pK_a value for that titration as indicated in the introduction. Enter these values on the report sheet, along with the average and standard deviation of the three best values.

2. Along with your report sheets, be sure to submit the printout of the graphs for each of the titrations.

DISPOSAL OF SOLUTIONS: COMBINE ANY LEFT OVER ACID WITH THE LEFT OVER BASE TO NEUTRALIZE, AND DISCARD THEM DOWN THE SINK WITH LOTS OF WATER TO DILUTE THEM.