Instructor Resources

By
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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.

PROCEDURE OVERVIEW

• the dropping buret is calibrated for drop size and the pH electrode is calibrated with buffers of 4, 7, and 10 pH

• four titrations of a 0.1 M solution of phosphoric acid of both equivalence point regions are accomplished with standardized 0.1 M NaOH.

• the exact volume for the first equivalence point is determined for each titration.

• the Ka1 value for each titration is determined from the pH at the half-equivalence point volume, and the average and standard deviation are obtained.

K_{a1} OF PHOSPHORIC ACID BY TITRATION

REPORT SHEETS:

NAME: _____   SECTION:_____   DATE: _____

Calibration: 1st _____   2nd _____   (drops/5 ml)

TITRATION DATA:

Trial #	1st der. vol.	2nd der. high vol.	2nd der. low vol.	2nd der. interp. vol.	2nd der. mmol NaOH	0.5 1st Equiv. vol.	pH > 0.5 Equiv. Vol.	pH < 0.5 Equiv. Vol.	pK_{a1} interp from pH	H_3PO_4 conc.
1										
2										
3										
4										
Ave. 1-4										
Std Dev.										
% error										

QUESTIONS FOR YOUR CONSIDERATION:

1. Show a sample set-up for the calculation of the 1st derivative interpolated volume. Do the calculations for all of the titrations in your lab notes (or on a spread sheet), and add the calculation results for all of the trials to the table above.

2. Show a sample set-up for the calculation of the pK_{a1} interpolated value from the pH of the volume to ½ of the first equivalence point volume, and then calculate the pH at that volume. Do the calculations for all of the trials in your lab notes (or on a spread sheet) and add them to the table above.

3. **In your lab notes**, (or on a spread sheet) calculate the exact concentration of each of the H_3PO_4 solutions you used in your titration and add them to the above table. Show a sample calculation below.

4. **Using the Column Statistics**, calculate the **Mean** (average) and standard deviation of all the titrations and add to the above table, then express your final average concentration as "Ave. value $\pm$ Std. Dev." in the space below.

5. According to Linus Pauling's rules for the strengths of oxyacids, what should be the Ka_1 and Ka_2 values for H_3PO_4?

6. How do your results agree with Pauling's values. If there is a significant difference, explain.

7. Explain why you were instructed to use the half equivalence point volume of the first ionization to determine the pK_a.

8. Why must one never pipet a liquid by sucking on the pipet by mouth?

9. Why is it necessary to rinse the buret or pipette with three rinses of the solution to be placed in it?

10. By discussing in detail what is happening to the pH near the equivalence point versus volume of titrant added, explain why it is necessary to take as small of volume increments as possible near the equivalence point.

K$_{a1}$ OF PHOSPHORIC ACID BY TITRATION

Tips and Traps

1. During the calibration of the pH probes, students may compare millivolt readings and become concerned that they may differ widely from system to system. Assure them that this is natural and is a function of differences in the nature of the pH electrodes. The values should be around 0 ± 100 millivolts if the pH probe is good.

2. You may find a wide variation in the quality of electrodes depending upon the manufacturer and/or age of the electrode. Some electrodes will reach equilibrium quite rapidly, while others may take a while. All electrodes should be checked out in advance to determine if they obtain equilibration within about 5 to 10 seconds. If not, the electrodes should be treated with an enzymatic cleaner, then soaked in an electrode conditioning solution, both of which can be obtained from Markson.

3. Since we are trying to determine the Ka1 of phosphoric acid, it is important to get the best calibration possible. Use new buffer solutions and allow adequate equilibration time with good stirring. In addition, allow a reasonable time for equilibration during the calibration procedure, and then use that same time interval for each measurement during the titration.

4. There is a tendency for students to leave the pH probe hanging out in the air between titrations. If the time between titrations is small, this probably won't matter much, but it is better to teach them good practice, and that is to store the probe in their buffer in a beaker placed at the back of the bench between titrations. There is less chance of breakage this way, and the probe is equilibrating at or near the equivalence point pH.

5. In between uses, all electrodes should be kept in a sealed container with the bulbs covered with the conditioning solution mentioned above.

K$_{a1}$ OF PHOSPHORIC ACID BY TITRATION

Suggested Answers

Calibration: 1st _____   2nd _____(drops/5 ml)

TITRATION DATA:

Trial #	1st der. vol. (ml)	2nd der. high vol. (ml)	2nd der. low vol. (mL0	2nd der. interp. vol. (ml)	2nd der. mmol NaOH	0.5 1st Equiv. vol. (ml)	pH > 0.5 Equiv. Vol.	pH < 0.5 Equiv. Vol.	pK$_{a1}$ interp from pH	H$_3$PO$_4$ conc. M
1	9.45	9.40	9.45	9.450	0.9436	4.178	1.290	1.210	1.248	0.0944
2	9.80	9.82	9.80	9.806	0.9806	4.903	1.540	1.340	1.374	0.0981
3	9.30	9.30	9.25	9.247	0.9247	4.624	1.510	1.450	1.451	0.0925
4	9.65	9.65	9.654	9.654	0.9650	4.827	1.540	1.340	1.381	0.0965
Ave. 1-4	9.55			9.539	0.953	4.633			1.364	0.0954
Std Dev.	0.22			0.24	0.02	0.33			0.084	0.002
% error	2.3			2.6	2.6	7.0			6.2	2.6

(5 points per question)

QUESTIONS FOR YOUR CONSIDERATION: (The data for these calculations was acquired using a volumetric buret, but the principles are the same.)

1. Show a sample set-up for the calculation of the 1st derivative interpolated volume. Do the calculations for all of the titrations in your lab notes (or on a spread sheet), and add the calculation results for all of the trials to the table above.

> *9.40 ml*   *+49.87*   *x = (9.45-9.40)(49.87-0)/(49.87-(-18.49)) = 0.036 ml*
> *9.40 + x ml*   *0*
> *9.45 ml*   *-18.49*   *Eq. Pt. volume = 9.40 + 0.036 = 9.436 ml*

2. Show a sample set-up for the calculation of the   pK$_{a1}$ interpolated value from the pH of the volume to ½ of the first equivalence point volume, and then calculate the pH at that volume. Do the calculations for all of the trials in your lab notes (or on a spread sheet) and add them to the table above.
> *1.21*   *4.50*   *x = (1.29-1.21)(4.718-4.50/(4.50 -(-5.00)) = 0.002*
> *1.21 + x*   *4.718*
> *1.29*   *5.00*   *pH @ ½ Eq. Pt. Vol = 1.21+0.002 = 1.212 = pKa1*

K$_{a1}$ OF PHOSPHORIC ACID BY TITRATION

Suggested Answers

3. **In your lab notes**, (or on a spread sheet) calculate the exact concentration of each of the H$_3$PO$_4$ solutions you used in your titration and add them to the above table. Show a sample calculation below.

$$\frac{(9.436 \ ml \ OH^-)(0.1 \ mmol \ OH^-)(1 \ mmol \ H^+)}{(1 \ ml \ \underline{OH^-})(1 \ mmol \ OH)(10 \ ml \ H^+)} \quad \frac{1}{} \quad = \quad 0.0944 \ M$$

4. **Using the Column Statistics**, calculate the **Mean** (average) and standard deviation of all the titrations and add to the above table, then express your final average concentration as "Ave. value ± Std. Dev." in the space below.

    0.0954 ±0.002

5. According to Linus Pauling's rules for the strengths of oxyacids, what should be the Ka$_1$ and Ka$_2$ values for H$_3$PO$_4$?

    Paulings rules indicate Ka1 should be about 10$^{-2, -4}$, and Ka2 about 10$^{-5, -9}$.

6. How do your results agree with Pauling's Values. If there is a significant difference, explain.

    If the Ka1 is about #.# x 10^{-2}, then the pKa1 should be about 3.#. The values obtained experimentally are an order of magnitude larger than that, indicating that there probably was a problem with the pH calibration. The actual values for H$_3$PO$_4$ are K$_{a1}$ = 7.5 X 10^{-3}, K$_{a2}$ = 6.2 X 10^{-8}, and K$_{a3}$ = 4.2 X 10^{-13}, which would give pKa1 as 4.1.

7. Explain why you were instructed to use the half equivalence point volume of the first ionization to determine the pK$_a$.

    At ½ the equivalence point volume, the [H$_3$PO$_4$] = [H$_2$PO$_4^-$] so that the log term goes to zero and pH = pKa1

8. Why must one never pipet a liquid by sucking on the pipet by mouth?

    Sucking on a pipet by mouth can cause the ingestion of chemicals into the mouth and or stomach, which can be very corrosive or toxic.

9. Why is it necessary to rinse the buret or pipette with three rinses of the solution to be placed in it?

    The buret has been stored filled with water. If the titrant is added directly to the buret without rinsing several times first, the concentration of the titrant will be diluted and you will not obtain the correct results for the titration.
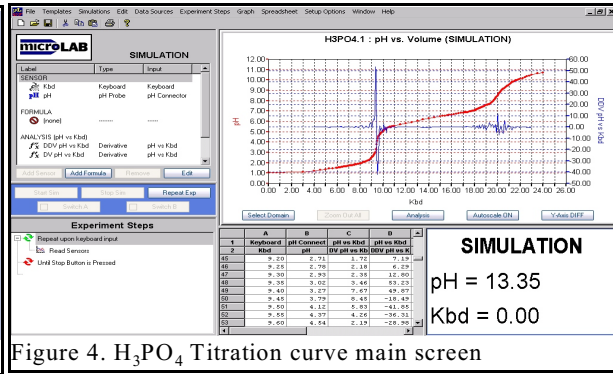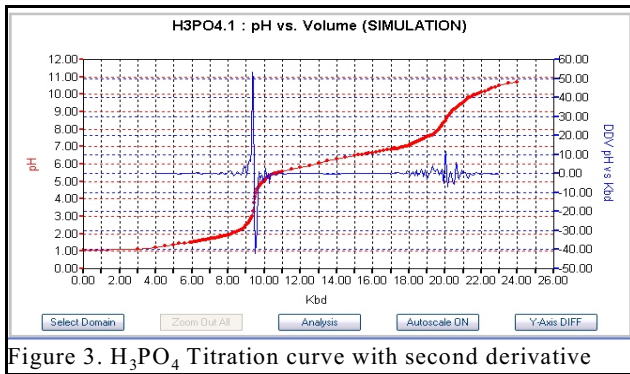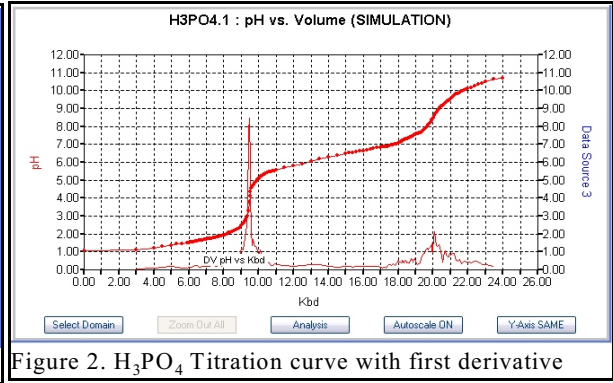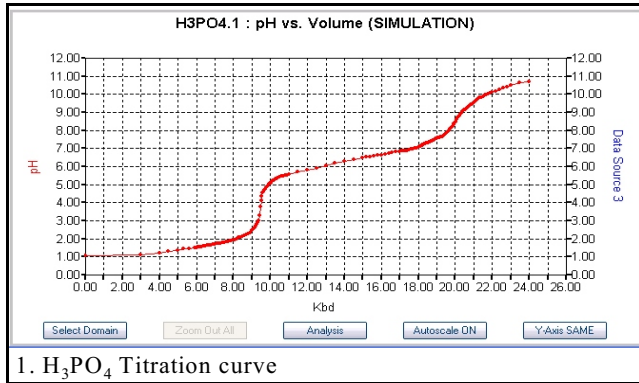
10. By discussing in detail what is happening to the pH near the equivalence point versus volume of titrant added, explain why it is necessary to take as small of volume increments as possible near the equivalence point, or if doing drop titrations, to slow the drop rate down significantly in the equivalence point region.

The pH changes very slowly during the titration until the titration approaches the equivalence point region. In this region, the [H$^+$] concentration begins to be very small by orders of magnitude, so that a small drop of titrant will cause a significant change in the [H$^+$], consequently the need for very small drops within the equivalence point region of the titration.

In doing a drop titration, the drop rate should be significantly slowed in the equivalence point region due to the rapid change of pH in that region. Since the pH electrode has a response time on the order of ten or more seconds, there needs to be time for the electrode to approximate equilibration before the next drop is added in order to get good pH readings.

K$_{a1}$ OF PHOSPHORIC ACID BY TITRATION

Sample Data

1. H$_3$PO$_4$ Titration curve

Figure 2. H$_3$PO$_4$ Titration curve with first derivative

Figure 3. H$_3$PO$_4$ Titration curve with second derivative

Figure 4. H$_3$PO$_4$ Titration curve main screen

The other three titration curves should be analogous to these.

K$_{a1}$ OF PHOSPHORIC ACID BY TITRATION

Laboratory Preparation (per student station)

EQUIPMENT:

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

1 - Dropping buret system   1 utility clamp for the dropping buret
1 - 5 ml pipet   1 - pipetting bulb
3 - 10 ml beakers   4 - 250 ml beakers
1 - magnetic stirrer with stirring bar   1 - ring stand
1 *MicroLAB* drop counter   1 - clamp for the counter
1 - pH probe with BNC connector
1 - *MicroLAB* interface and two *MicroLAB* programs (*Drop Counter Calibration* and one of the titration programs, as per the 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.

- 150 ml of 0.100 M NaOH solution
- 30 ml of 0.100 M H$_3$PO$_4$ solution
- 15 ml of pH 4, 7 and 10 buffer solutions per pair of students in a 10 ml beaker.

CAUTIONS OF CHEMICAL HAZARDS:

- H$_3$PO$_4$ 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.

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