

# K<sub>a1</sub> OF PHOSPHORIC ACID BY TITRATION (#10.7)

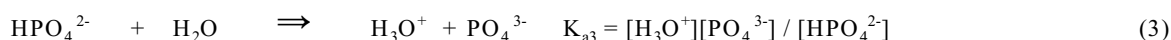
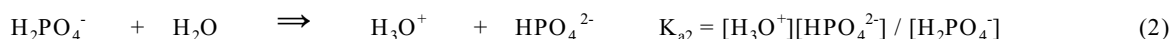
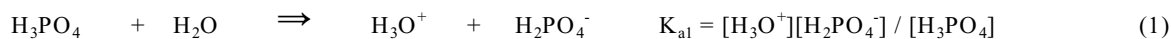
By Dale A. Hammond, PhD, Brigham Young University Hawaii

## Learning Objectives

- 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<sub>3</sub>PO<sub>4</sub>, has three ionizable hydrogen atoms; it is a *triprotic* acid, each step having a distinctive ionization constant expression and numerical value as:



Phosphoric acid is a weak acid in its first ionization step and is about 10<sup>-5</sup> weaker acid in the second and very weak in the third ionization, again by about 10<sup>-5</sup>. Ionization is fairly complete in the first step, however we still have some H<sub>3</sub>PO<sub>4</sub> molecules in solution, and the concentration of the H<sub>3</sub>O<sup>+</sup>, contributed by this ionization is enough to make the solution significantly acidic. However, the second dissociation constant of H<sub>3</sub>PO<sub>4</sub> is quite small and there is little H<sub>3</sub>O<sup>+</sup> 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 reasonably be able to differentiate them. Since the equivalence points for H<sub>3</sub>PO<sub>4</sub> differ by about 10<sup>-5</sup>, the first two equivalence points are readily determined. The third equivalence point is so small it is unobservable in aqueous titrations.

The derivation of the Henderson-Hasselbalch equation is given  $\text{pH} = \text{p}K_{a1} + \log\left\{\frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}\right\}$  (4)

At exactly one-half the equivalence point volume, [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>] = [H<sub>3</sub>PO<sub>4</sub>], the log term goes to zero, and the pH = pK<sub>a1</sub>. Thus, the first ionization constant, K<sub>a1</sub>, can easily be determined from the half equivalence point volume corresponding to the first ionization

Slope is defined, as are also the first and second derivatives to assist in determining the exact equivalence point of the titration.

**Pauling's Rules:** Pauling's rules for acid strength of oxyacids is discussed and applied to the acid strengths of the three dissociations of H<sub>3</sub>PO<sub>4</sub>.

## Procedure:

- The pH probe, *MicroLAB* interface, computer and associated software will serve as the associated electronics and readout device of the pH meter.
- The pH probe is calibrated using buffer solutions of 4, 7 and 10 pH.
- The drop counter is calibrated to determine the volume per drop.
- At least three titrations of H<sub>3</sub>PO<sub>4</sub> are obtained to be able to calculate an average and standard deviation on the data.

## Data Analysis

Guidance is provided for the necessary calculations and formation of the derivatives to obtain the desired data.

## Instructor Resources Provided

- Sample Report Sheets providing the format to organize the data collection with sample data.
- Questions to consider, answer and turn-in with suggested answers.
- Tips and Traps section to assist the instructor with potential problems and solutions.
- Sample *MicroLAB* screen shots and graphs.
- Laboratory preparation per student station.

