

## CHM 106

### Potentiometric Titration of Phosphoric Acid

#### BACKGROUND

Potentiometric titrations are a useful method of determining unknown concentrations in many different types of chemical systems. They may be employed in redox chemistry by monitoring the reduction potential of the titration flask as titrant is added, or they may be used in acid-base chemistry where the pH of the titration flask is monitored as acid or base is added.

Experimentally, a pH meter relates a voltage from the probe to pH, so these techniques are actually quite similar. A detailed examination of potentiometric acid-base titrations is given in section 15.4 (pages 729-744) of the textbook.

In this lab, we will conduct a potentiometric titration of a solution of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) of unknown concentration. We will determine the concentration of the phosphoric acid solution and the values for the first two acid dissociation constants. We will also examine indicator selection in titrations.

#### MATERIALS AND REAGENTS

250 mL beaker, 10 mL pipet, buret, pH meter, magnetic stirplate and stirbar  
0.100 M NaOH,  $\text{H}_3\text{PO}_4$  unknown, pH 4 and 7 reference solutions, indicators

#### PROCEDURE

This lab will be conducted in groups but the lab report must be completed and submitted individually.

Pipet 10.00 mL of the  $\text{H}_3\text{PO}_4$  solution into a clean, dry 250 mL beaker. Add 40 mL of distilled water to the beaker. Place the 250 mL beaker on a magnetic stirrer and add a stirring bar. Fill a clean buret with 0.100 M NaOH solution so that it is exactly at the 0.00 mL mark and position over the beaker.

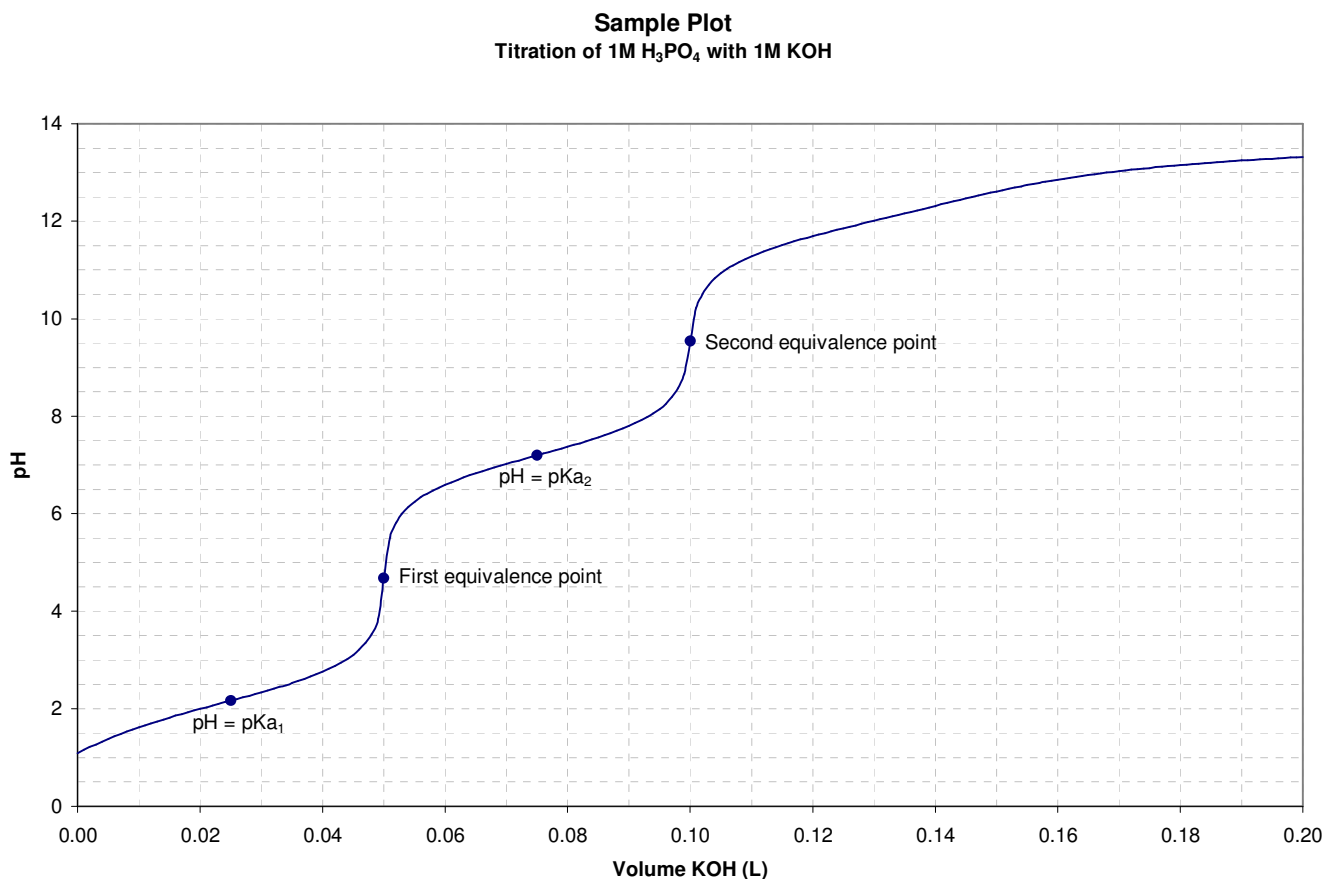
Calibrate a pH meter using reference buffers of pH 4.0 and pH 7.0. Using an apparatus clamp, position the pH electrode in the 250 mL beaker so that the probe is submerged in the solution but is not in any danger of being struck by the stirbar. Begin stirring the solution at a medium speed.

Add a couple drops of indicator solution. Each group will use a different indicator. Record the pH of the solution. Add about 0.5 mL of NaOH from the buret. Record accurately the volume of base added and the pH of the solution. Repeat, adding base in 0.5 mL increments and recording the pH until all 50 mL of base have been added. While adding base, observe the color of the indicator in your titration flask and record the endpoint of the titration, according to your indicator, along with the appropriate data points.

Be sure to obtain the observations on the indicator color change from other groups before you leave the laboratory.

## DATA ANALYSIS

Using spreadsheet software, plot the pH of the titration flask versus the volume of NaOH added. You should obtain a plot similar to the one shown below, but your values will be different because the concentrations and amounts used in the lab are different from this example.



Since phosphoric acid is a polyprotic acid, we will observe one equivalence point for each successive ionization. However, since the  $K_a$  for this third ionization ( $1.259 \times 10^{-12}$ ) is close in magnitude to the ion product constant of water ( $1.00 \times 10^{-14}$ ) the third equivalence point will be obscured on the titration curve.

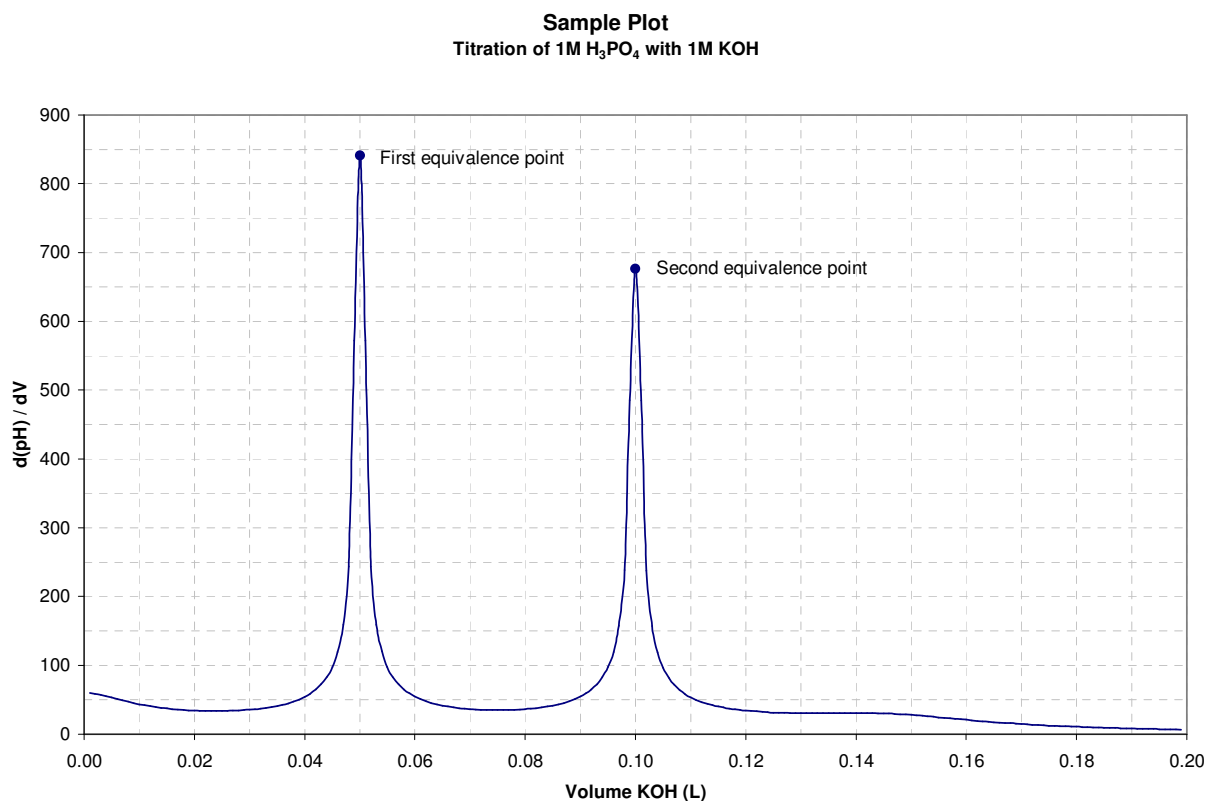
We will recall that the steep vertical regions correspond to the equivalence points and at half the volume of an equivalence point (or the volume halfway in between equivalence points) is the point at which the pH of the solution is equal to the  $pK_a$  for that dissociation. However, it is difficult to determine exactly where on the vertical region the equivalence point lies.

Observe that near the equivalence point, the slope of the titration curve is very high. Prior to the equivalence point, the slope of the titration curve is increasing, and after the equivalence point, the slope begins to decrease. Mathematically, the point at which the slope of a curve stops increasing and begins to decrease is called an inflection point. We can take advantage of mathematics to make it easier to determine precisely where the equivalence point lies.

In your spreadsheet, calculate the slope between each pair of data points. Mathematically,

$$\text{slope} = \frac{\text{pH}_2 - \text{pH}_1}{V_2 - V_1} = \frac{d(\text{pH})}{dV}$$

Where  $\text{pH}_1$  and  $\text{pH}_2$  are the pH values of successive data points and  $V_1$  and  $V_2$  are the corresponding volumes of NaOH. This slope of the curve that we have calculated is called the first derivative and is designated as  $\frac{d(\text{pH})}{dV}$  because it is the rate of change of the pH with respect to volume. Prepare a plot of the first derivative of pH (slope of pH vs V) versus volume of NaOH added. You should obtain a plot similar to the one shown below:



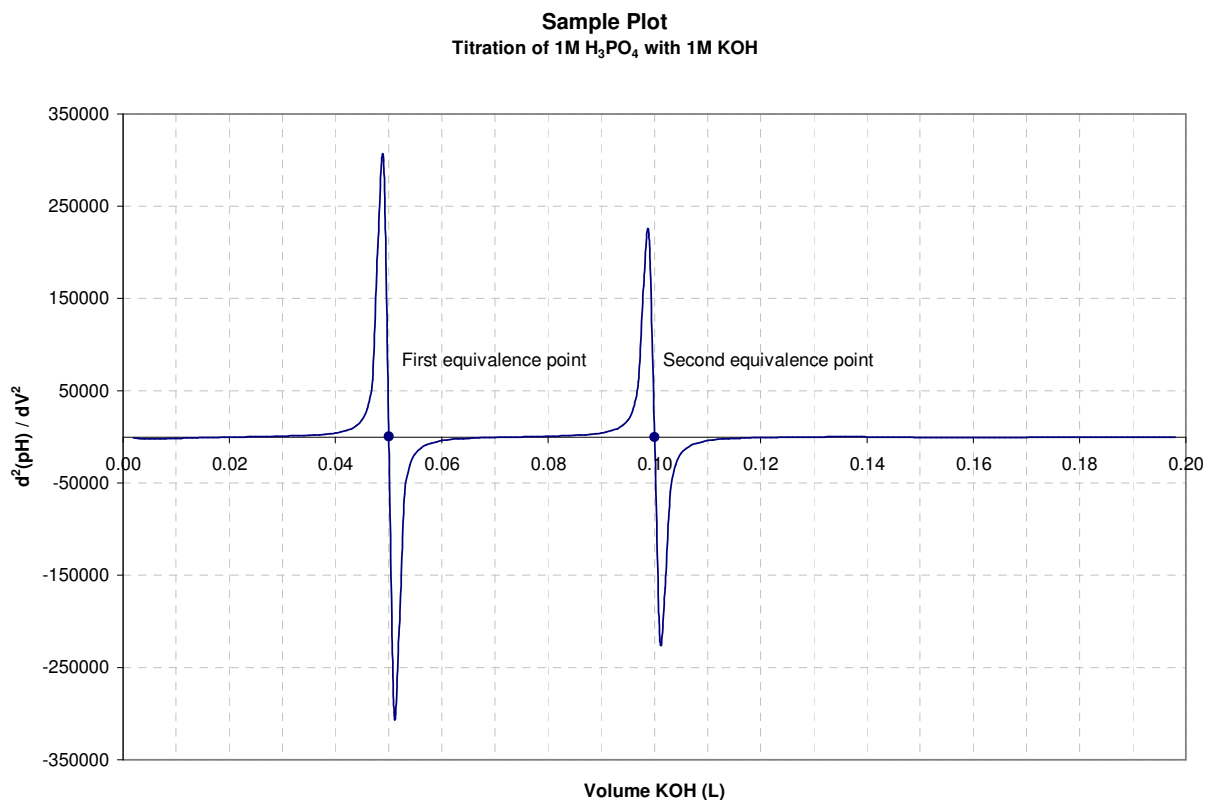
Calculus tells us that when a function passes through an inflection point, its derivative will pass through a local maximum or minimum. Notice that it is considerably easier to find the locations of the equivalence points in the plot of the first derivative. However, due to experimental errors in the data we have, the tops of the peaks in this plot may be broadened, and still somewhat difficult to locate the precise maximum. We can once again turn to mathematics for help.

Observe that the slope of the derivative plot is positive before reaching the maximum because the value of the derivative is increasing. At the maximum, the slope of the derivative is zero, and past the maximum the slope of the derivative plot is negative because the value of the derivative is decreasing. We can thus examine the derivative (slope) of the derivative plot and when it equals zero, we will know precisely the location of the equivalence point and the corresponding volume of NaOH at the equivalence point.

In your spreadsheet, calculate the slope of the derivative between each set of data points. Mathematically,

$$\text{slope} = \frac{\text{pH}'_2 - \text{pH}'_1}{V_2 - V_1} = \frac{d^2(\text{pH})}{dV^2}$$

where  $\text{pH}'_1$  and  $\text{pH}'_2$  are successive values of the derivative (not the pH itself) and  $V_1$  and  $V_2$  are the corresponding volumes of NaOH. You should obtain a plot similar to the following:



Now it is unambiguous where the equivalence point lies because there is a very sharp transition of the second derivative plot from positive to negative and an obvious value where it equals zero. This value is the volume of NaOH at the equivalence point. From your second derivative plot, determine the volume of sodium hydroxide at the first and second equivalence point.

Once we know the volume of sodium hydroxide at each equivalence point, it is a simple matter to find the  $\text{pK}_a$  values for each dissociation. Refer to the first plot you constructed. At a volume equal to half the equivalence point (or halfway between equivalence points),  $\text{pH} = \text{pK}_a$ . From your first plot, determine the values of  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$  for phosphoric acid. Given that the literature values are  $\text{pK}_{a1} = 2.148$  and  $\text{pK}_{a2} = 7.198$ , calculate a percentage error for each measurement.

We can also use this data to determine the concentration of H<sub>3</sub>PO<sub>4</sub>. At the first equivalence point, the reaction  $\text{H}_3\text{PO}_4(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{H}_2\text{PO}_4^-(aq)$  is complete. Since we know the concentration (0.100 M) of NaOH, the volume of NaOH at the equivalence point, and the

volume of  $\text{H}_3\text{PO}_4$  used, we can calculate the concentration of phosphoric acid. Similarly, at the second equivalence point, the reaction  $\text{H}_3\text{PO}_4(aq) + 2\text{OH}^-(aq) \rightarrow 2\text{H}_2\text{O}(aq) + \text{HPO}_4^{2-}(aq)$  is complete so we can do similar calculations. These calculations should result in the same value, but they will probably be slightly different due to experimental error. Determine the value of the concentration of phosphoric acid using data from each equivalence point. Average their values and report this average as the value of the concentration of phosphoric acid.

Mark the end point of each titration, according to the indicators used, on your plot of pH versus volume of NaOH. In your discussion, comment on whether each indicator was appropriate for the titration (Was the end point close to the equivalence point?) and comment on the implications of the end point of each indicator on doing the calculations for the titration. Calculate the concentration of phosphoric acid according to each indicator's end point, and calculate a percentage error between the end point and the appropriate equivalence point.

## QUESTIONS

1. Would bromothymol blue ( $\text{pK}_a = 7.1$ ) be an appropriate indicator for the titration of phosphoric acid samples? Explain.
2. How does buffering in a titration of a weak acid or weak base affect the shape of the titration curve when compared to the titration curve of strong acid with strong base? Explain.