

POTENTIOMETRIC ANALYSIS OF A HCl ! H₃PO₄ MIXTURE

DISCUSSION: This analysis will acquaint you with potentiometric methods of analysis using the glass electrode and pH meter. The pH meter in conjunction with the glass electrode is the method of choice for the direct measurement of pH, or as a means to obtain data to construct a titration curve. In this analysis, a mixture of two acids will be titrated to determine the concentration of each acid. A titration curve will be constructed which will locate the exact equivalence points. The glass electrode, which detects hydronium ion activity, allows the analysis of mixtures of acids in which color ranges of conventional indicators may overlap. Also, the glass electrode can be used with colored solutions and with analyses that take place in nonaqueous solvents.

The Potentiometric Titration:

A potentiometric titration employs the measurement of an electrical potential (a voltage) as a means to detect the equivalence point of a titration. This technique can be applied to all types of analyses which involve titrimetric methods. The electrical potential is produced by a galvanic cell, and the magnitude of the potential depends on the activities (concentrations) of the solutes in the cell solutions. The relationship between potential and activity is the basis for potentiometry as an analytical tool. In many cases a cell can be designed to respond to a single ionic species, like the potassium ion, sodium ion or the hydronium ion. In a potentiometric titration, the cell is composed of an *indicator electrode* (which is responsive to the analyte activity, the hydronium ion in our case) and an external *reference electrode* (an electrode which produces a constant potential). The electrical potential between the two electrodes is a measure of the analyte activity. The role of the pH meter is to measure this potential, amplify it and display the result on a meter.

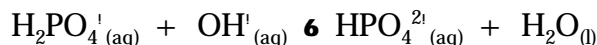
The commercial glass electrode is used to measure hydronium ion activity and, with the meter, pH. It consists of glass tube with a thin-walled glass bulb on one end containing a solution of fixed hydronium ion activity, usually 0.1 M HCl_(aq) and an *internal* reference electrode, the silver|silver chloride cell, Ag_(s)|AgCl_(s). When the bulb is immersed in a solution, an electrical potential develops across the glass membrane in response to the hydronium ion activity in the external solution. The potential is measured

Phosphoric acid is a tribasic acid. Its K_a values are approximately 10^{-3} , 10^{-8} and 10^{-13} . Because these K_a 's are sufficiently separated, H_3PO_4 can be titrated with a strong base to give distinct and well defined end points indicating the neutralization of the first and second protons. The pH values at the two equivalence points are:

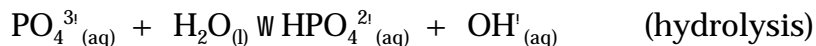
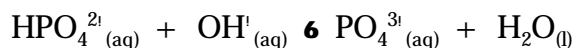
At the first equivalence point: **pH = 4.7**



At the second equivalence point: **pH = 9.3**



Neutralization of the third proton of phosphoric acid does not produce an appreciable break in the titration curve. This is ultimately because K_{a3} is very small and acids with small K_a 's produce small breaks, (remember Figure 1), and because K_{a3} is so small, the basicity (proton accepting ability) of the phosphate ion is large, and it undergoes hydrolysis producing hydroxide ion.



So with phosphoric acid, you can expect to see only two well defined breaks in its titration curve, the first centered at a pH of 4.7 and the second at approximately a pH of 9.3.

Here is another interesting fact that will be important in this analysis. If a 0.05 M solution of $HCl_{(aq)}$ is titrated to a pH of approximately 4.7 (the pH of the 1st eq. pt. of H_3PO_4), the hydronium ion concentration from the $HCl_{(aq)}$ yet to be neutralized will be 2×10^{-5} M (the antilog of -4.7). The fraction of the initial concentration of $HCl_{(aq)}$ remaining at this pH is about 0.04%.

$$\frac{2 \times 10^{-5} \text{ M}}{5 \times 10^{-2} \text{ M}} \times 100\% = 0.04\%$$

At pH 4.7 there is such a small fraction of $HCl_{(aq)}$ remaining that if a mixture of $HCl_{(aq)}$ and H_3PO_4 are titrated together to a pH of approximately 4.7, all the $HCl_{(aq)}$ can be considered neutralized *and* all of the H_3PO_4 will have been converted to $H_2PO_4^-$ as its first proton is neutralized. As the titration continues, the second proton is

neutralized, H_2PO_4^- being converted to HPO_4^{2-} , in the span from the first to the second equivalent points.

The titration curve of a mixture of HCl and H_3PO_4 would be expected to appear as shown in Figure 2.

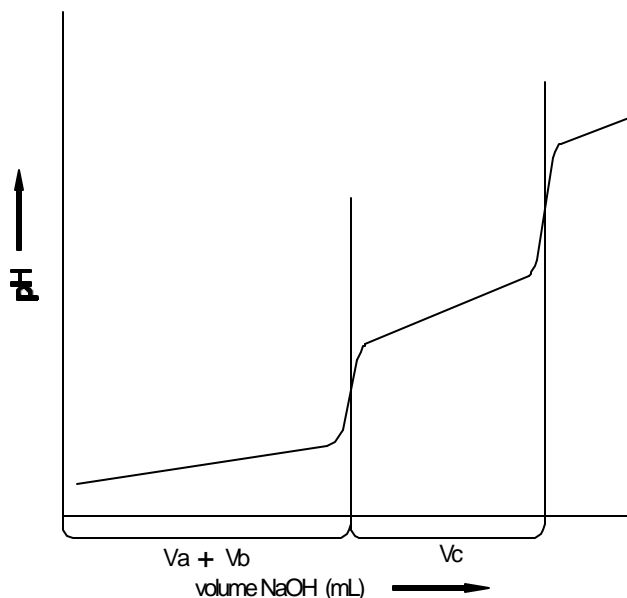


Figure 2 The titration curve for $\text{HCl}_{(\text{aq})}$ and H_3PO_4 titrated with NaOH

To clarify: V_a is the volume of NaOH required to neutralize the $\text{HCl}_{(\text{aq})}$; V_b is the volume of base required to neutralize the first proton of H_3PO_4 forming H_2PO_4^- ; and V_c is the volume of base required to convert the $\text{H}_2\text{PO}_4^{2-}$ to HPO_4^{2-} . V_b must equal V_c . In the titration, V_c is determined from the titration curve and subtract-

ed from the sum $V_a + V_b$ to give the volume of base required to titrate the HCl, V_a . Thus, the two concentrations, $\text{HCl}_{(aq)}$ and H_3PO_4 , can be determined in a mixture of the two.

In this analysis you will be given a mixture of hydrochloric and phosphoric acids of unknown concentrations. Your task will be to determine the concentrations of these acids in the mixture using a potentiometric titration with standard $\text{NaOH}_{(aq)}$.

**PREPARATION
OF REAGENTS:**

Standard NaOH: Prepare one liter of approximate 0.12 M carbonate-free NaOH solution by carefully adding the calculated volume of concentrated sodium hydroxide (19.1 M) to approximately 1 liter of previously boiled and cooled deionized water in a clean bottle. If concentrated NaOH is not available, dissolve the calculated mass of solid NaOH, weighed out on a *top loader* balance, in the appropriate volume of prepared water.

Primary Standard KHP: Dry approximately 0.5 g of Potassium Hydrogen Phthalate (KHP) for 1 to 2 hours at 110°C. To save time, this should be done before lab starts.

The Sample of Unknown: To receive the unknown acid mixture, provide the instructor with a clean (no labels) and relatively dry, 250 mL screw top bottle.

EXPERIMENTAL Standardization of NaOH: Sodium hydroxide may be standardized **PROCEDURE:** by titration against KHP using phenolphthalein as the indicator, or it may be titrated potentiometrically. Your instructor will tell you which method to use.

If you standardize the NaOH against KHP, follow the procedure described in the Preparation of Standard Sodium Hydroxide experiment. If you standardize NaOH potentiometrically, follow the instructions given below. Only one trial need be done.

1. Weigh accurately, 0.4 g of KHP into a clean 250 mL beaker. Dissolve the solid in approximately 100 mL of deionized water.
2. Calibrate the pH meter according to the instructions in Appendix A-3.
3. Set up the titration apparatus as shown below in Figure 3 on the following page.

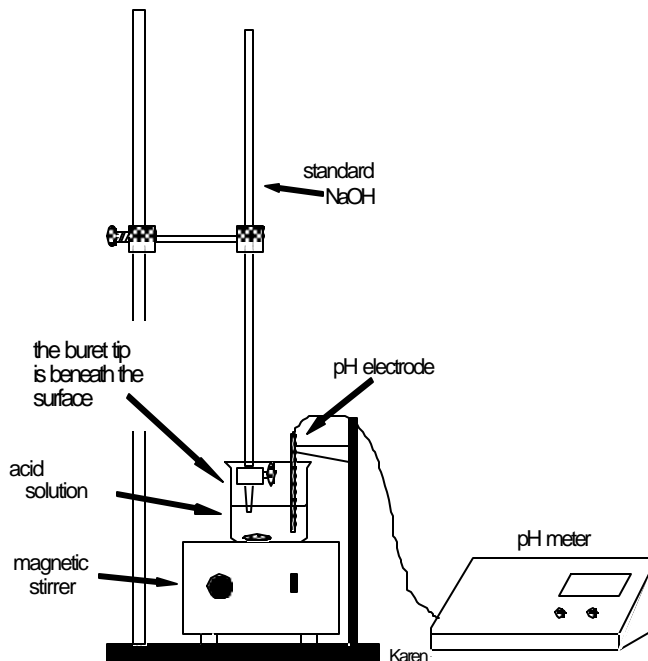


Figure 3 Equipment setup for the potentiometric titration.

- Place the electrode in the solution, ensuring the thin-walled glass bulb is beneath the surface of the solution but not immersed so deeply that it contacts the stir bar. Adjust the stirrer to achieve a slow, continuous stirring rate without spattering, then position the buret containing the NaOH solution over the beaker containing the KHP (or acid) solution.
- Begin the procedure by measuring the *initial pH* of the solution (at NaOH volume of 0.00 mL), then begin the titration. Record the pH of the solution after additions of NaOH at 1 mL intervals (approximately). Record the exact volume of NaOH added each time in your notebook followed by the pH of the analyte solution.

Record data in your notebook in two columns, like this:

Vol. NaOH added (mL)	pH of analyte solution
S))))))))))))))))))))))))))	
0.00 mL	3.85 (use actual values)
1.05	3.96
2.04	4.09
etc.	etc.

- This titration will proceed slowly, especially as you get near the equivalence point. As you get close to the equivalence point, you will notice that larger changes in pH occur with smaller and

smaller additions of base. Once you observe this happening, add base in very small volumes from this point on, *a drop or two at a time*. Once you titrate through the equivalence point (signaled by a large change in pH), larger increments of titrant can again be added. Continue the titration until a pH of about 12 is reached.

Titration of the Unknown Acid Mixture:

1. Take the sample for analysis by pipeting 50.0 mL of the unknown acid mixture into a clean 250 mL beaker. Dilute the sample with approximately 100 mL of deionized water, and place a Teflon[®] coated stirring bar in the solution.
2. Proceed with the potentiometric titration as described above, beginning with step 2.
3. Record the initial pH in your notebook, then record the volume and pH after each 2 mL addition of base. When the pH reaches 3, reduce the volume of base you add each time so more readings can be taken as the pH climbs to 3.5. Estimate from each pH change which follows and addition of base whether the next volume increment must be made smaller to avoid running over the equivalence point. Once the pH reaches 3.5, add base in 0.10 mL increments (2 drops) or less until the change in pH with each addition becomes very small which should be evident at a pH of about 5.5.
4. Once you have passed through the first break in the titration curve, at a pH of about 5.5, add 3 mL increments of base until you reach a pH of 7.8. From this point on, add smaller increments of base as before. As the pH approaches 8.3, add base in 0.10 mL increments (or less) until the change in pH with each addition becomes very small following the second break which should be evident at a pH of about 10.3. Take at least 4 pH readings beyond the second break at 2 mL increments.
5. At the conclusion of the titration, remove the electrode from the solution, rinse it thoroughly with deionized water and cover the end of the electrode with the protective plastic cap. Turn off the pH meter.

CALCULATION Potentiometric Standardization of NaOH:

1. Generate a graph using Quattro Pro[®], plotting pH versus the Volume NaOH (mL). The instructions for graphing data are in Appendix A-4. Note the approximate location of the equivalence point, then make an additional *expanded graph* by plotting

the data for a volume span of ± 2 mL on either side of the estimated equivalence point. Using this same expanded data set, plot the *first derivative curve* and determine the end point graphically from the plot. Instructions for generating the first derivative plot are given at the end of this section.

- Using the "pH" and "Volume NaOH" data, generate a **Gran plot** by plotting ($V_b \times 10^{\text{pH}}$) versus V_b , where V_b is the volume of base (in mL) which is plotted on the horizontal axis. The values of V_b should be those comprising the last 10% of volume added before the equivalence point volume, V_{eq} . (Plot the volumes that range from $0.9 V_{\text{eq}}$ to V_{eq}). Extrapolation of the *best fit line* drawn through the points will give the true value of V_{eq} . The *slope* of the line equals $-K_a$ for KHP.
- Calculate the molarity of NaOH using the volume of NaOH required to reach the equivalence point, V_{eq} , *obtained from the first derivative plot*. Record your results on the Report Sheet.

Concentration of Acids in the Unknown Acid Mixture:

Generate the complete titration curve for the mixed acid unknown using Quattro Pro[®], (see Appendix A-4). Plot an expanded 1st derivative for *both equivalence points*. Calculate the molarity of each acid in the unknown and complete the Report Sheet.

WHAT YOU ARE TO SUBMIT: The table of titration data used to generate titration curves.

TO SUBMIT: *Six graphs*, including: a) the Gran plot, b) the two complete titration curves, and c) the three expanded first derivative curves. Indicate the equivalence point volumes, V_{eq} , on the expanded first derivative curves.

- The Report Sheet.

Supplemental Instructions for Using Quattro-Pro® 3.0:

How to Prepare A First Derivative Plot: Follow the instructions given above to enter the titration data into the spreadsheet. Enter the *volume NaOH* data in column A and the corresponding *pH* data in column B.

1. Move cursor to cell C1 then press the key combination ctrl-W and enter 22 then press ENTER, ³. Type in the line: First derivative calculations in cell C1. Set the cursor in cell C2 and enter the formula:

$$(b2! b1)/(a2! a1)$$

Note: this formula will calculate) pH ÷)V.

(continues)

2. Move cursor to cell D1 then press the key combination ctrl-W and enter 22 then press ENTER, ³. Type in the line Average volume NaOH in cell D1. Set cursor in cell D2 and enter the formula:

$$(a_2+a_1)/2$$

Note: this formula calculates the average volume of NaOH.

3. To copy these formulas into each of the remaining cells to calculate the rest of your data, press slash (/) to get the main menu, then select **EDIT** followed by Enter, ³. Select **COPY**, ³.
4. For **Source block of cells:** input C2 .. D2, ³.
5. For **Destination for cells:** input C2 .. Dn (where n is the number corresponding to next-to-last cell number used by the titration data), ³. Both C and D columns should fill with the appropriate calculated values.

How To Print Data: Return to the main menu by pressing the ESC key until the main menu appears. Select **Print**, ³. Select **Block**, ³. Type A1..Dn, (where n is number of the last cell), ³. Select **Spreadsheet Print**, ³. Select **Go**, ³.

How To Graph Titration and 1st Derivative Curves: Follow the instructions for graphing data with Quattro Pro[®] found in Appendix A-4.

To graph the *titration curve*, use the data in column A for the x-axis and that in column B for the 1st Series values (y-axis). Customize the x-axis by moving the cursor to **x-axis**, ³. Choose **manual**, ³. Make **increment**, ³, 2. Make **number of ticks**, 0. Leave the y-axis on automatic. To graph the 1st Derivative curve along with the titration curve, make column C the 2nd Series. "Customize" Series 1 to use symbols and lines (both). "Customize" Series 2 to use symbols only.

To graph the expanded *1st Derivative curve*, use column D for the x-axis values and column C for the 1st Series values (y-axis). Expand column D volumes so that 1 to 1.5 mL fills the graph. Customize the x-axis by moving the cursor to **x-axis**, ³. Choose **manual**, ³. Make **increment**, ³, 0.05. Make **number of ticks**, ³, 1. Leave the y-axis on automatic. Customize the graph to use "symbols" only.

REPORT SHEET:

**POTENTIOMETRIC ANALYSIS OF
A HCl : H₃PO₄ MIXTURE**

 Name _____ Date: _____ Sample No.: _____
 Please print; last name first

Standardization of NaOH : Titration Against KHP

	Trial 1	Trial 2	Trial 3	Trial 4
mass of KHP				
volume NaOH				
M_{NaOH}				

Average molarity of NaOH (4 sig. figs.): _____

Circle all values used to determine the average molarity of NaOH.

Standardization of NaOH: Data from the Gran and First Derivative Plots

From the Gran Plot	$V_{\text{eq}} =$	$K_a(\text{KHP}) =$
From the First Derivative Plot	$V_{\text{eq}} =$	
M_{NaOH} (calculated using V_{eq} from the first derivative plot)	$M_{\text{NaOH}} =$	

Name _____ Date: _____ Sample No.: _____
Please print; last name first

Analysis of the Mixed Acid		
	Trial 1	Trial 2 (if needed)
volume of mixed acid taken for analysis		
volume of NaOH to reach <i>first</i> eq. pt. from 1 st deriv. plot		
volume of NaOH to reach <i>second</i> eq. pt. from 1 st deriv. plot		
M_{HCl}		
$M_{\text{H}_3\text{PO}_4}$		

Show all calculations for one trial on the back of this page.