
Experiment 8: Quantitative Determination of Potassium Acid Phthalate (KHP) by an Acid-Base Titration

De Jesús M. A.; Vera M.; Padovani J. I. (2010); University of Puerto Rico; Department of Chemistry; P. O. Box 5000, Mayagüez, P. R. 00681.

PURPOSE

Determine the percent of potassium acid phthalate (KHP) in an unknown sample by means of an acid base titration with NaOH. Construct an acid-base titration curve to estimate the titration error of the analysis.

THEORY

According to the USP <541> a **direct titration** is the treatment of a soluble substance, contained in solution in a suitable vessel (**the titrate**), with an appropriate standardized solution (the titrant), the endpoint being determined instrumentally or visually with the aid of a suitable indicator. The titrant is added from a suitable buret and is so chosen, with respect to its strength (normality), that the volume added is between 30% and 100% of the rated capacity of the buret. [NOTE—Where less than 10 mL of titrant is required, a suitable microburet is to be used.] During a **titration** the chemical reaction of interest occurs by the addition of small increments of a reagent (**the titrant**) of known concentration (**a primary or a secondary standard**) to a solution of the analyte up to the point of chemical equivalence. The endpoint is approached directly but cautiously, and finally the titrant is added dropwise from the buret in order that the final drop added will not overrun the endpoint. The amount of the substance being titrated can be calculated from the volume, the normality or molarity factor of the titrant, and the equivalence factor for the substance under study. In any titration, a **primary standard** is used directly or indirectly to determine the concentration of the analyte. The accuracy of the method is highly dependent on the characteristics of this compound. Some of the **desirable properties** of a primary standard are:

- a. High Purity
- b. Stability
- c. Non hygroscopic
- d. Low cost
- e. Reasonable solubility in the titration medium
- f. High formula weight to minimize weighing errors

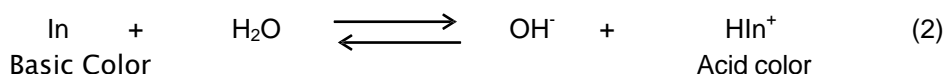
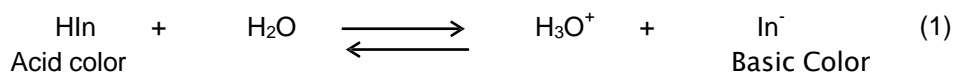
The number of substances that meet these criteria is very limited. Therefore, sometimes it is necessary to use **secondary standards**, whose purity, or concentration, is determined by titrating them against a standard solution, or by any other means of chemical analysis.

The volume of titrant required to complete the reaction is used to determine the amount of analyte present in the unknown sample. The titrant is usually delivered from a **buret**, which consists of a graduated cylinder with a stopcock at the end (**Experiment 3**). Burets are designed to deliver accurately known volumes of titrant at a given temperature. Each addition of titrant should be quickly consumed, until the reaction is completed. The point where the stoichiometric analytical amount of titrant is chemically equivalent to the amount of analyte reacted is defined as the **equivalence point**. Several methods are used to estimate the equivalence point. These include a change in color for an indicator, changes in the potential between a pair of electrodes, and changes in the absorbance of light during the reaction.

The simplest and most convenient method by which the equivalence point may be determined is with the use of indicators. These chemical substances, usually colored, respond to changes in solution conditions before and after the equivalence point by exhibiting color changes that may be taken visually as the endpoint, a reliable estimate of the equivalence point. In this experiment, we will focus our attention to the use of **acid-base indicators** to determine the end point of a titration. An acid-base indicator is an organic compound whose color changes at pH values near its pK_a or pK_b . In order to be efficient, the indicator should exhibit a color change at a volume near the equivalence point. The volume at which the change in

color occurs is called the **end point** of the titration. The equivalence point is the ideal or theoretical one, but the physical change in color occurs at the end point. The difference between the end point and the equivalence point is called the **titration error**. By choosing the appropriate indicator, the end point can be observed very close to the equivalence point and the titration error is insignificant.

Typically, acid-base indicators are high molecular weight organic acids and bases whose protonated and un-protonated species exhibit different colors. This change in color is due to internal structural changes that occur with the dissociation or association processes. The color changes for an acid-base indicator can be described by the following equilibrium:



In both cases, the colors of the basic and acid forms of the indicator are different. Since the human eye is not very sensitive to color differences in a solution containing both the acid and basic forms of the indicator; the color change has to be large enough to be easily observed. The useful range of an acid-base indicator can be estimated from its equilibrium constant expression as described by the ratio of the concentrations of $[\text{In}^-]/[\text{HIn}]$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_a}{[\text{H}_3\text{O}^+]} \quad (3)$$

where the useful range is:

$$\text{(Acid color)} \quad \frac{1}{10} \geq \frac{[\text{In}^-]}{[\text{HIn}]} \leq \frac{10}{1} \quad \text{(Basic color)} \quad (4)$$

This relationship corresponds to:

$$\begin{array}{l} \text{pH} = \text{p}K_a - 1 \text{ for the acid color; } \text{pH} = \text{p}K_a + 1 \text{ for the basic color} \\ \text{Thus, the pH range} = \text{p}K_a \pm 1. \end{array} \quad (5)$$

Obviously, this relationship provides only a general trend, since humans differ significantly in their ability to discriminate among colors. Properties of the most commonly used acid-base indicators are included in **Table 1**.

Table 1: Properties of some Acid-Base Indicators at 25°C in Aqueous Solution.

Indicator	pH Range	pka	Acid Form	Base Form
Alizarin yellow R	10.1-12.0	11.0	yellow	red
Bromcresol green	3.8- 5.4	4.7	yellow	blue
Bromothymol Blue	6.0- 7.6	7.1	yellow	blue
Cresol purple	7.4- 9.0	8.3	yellow	purple
Methyl yellow	2.9- 4.0	3.3	red	yellow
Methyl orange	3.1- 4.4	4.2	red	yellow
Methyl red	4.2- 6.2	5.0	red	yellow
Methyl violet	0.0- 1.6	0.8	yellow	blue
Phenol red	6.4- 8.0	7.4	yellow	red
Phenolphthalein	8.0- 9.8	9.7	colorless	red
Thymol blue	8.0- 9.6	8.9	yellow	blue

To determine the **titration error**, we may use the **back titration** technique, in which the volume of titrant added in excess is determined by titrating it with a standard solution. The error may also be determined by

monitoring the pH of the solution as a function of the volume of titrant, using a pH electrode. The data is used to plot a graph of pH vs. volume of titrant. The equivalence point occurs at the steepest point of the plot (**Figure 1a**). The equivalence point can also be estimated as the maximum of a first derivative (slope of titration curve) plot of pH vs. volume of titrant (**Figure 1b**). These data are prepared by using Excel or any other spreadsheet software (**Figure 2**). The titration error is the difference between the end point and the equivalence point volumes.

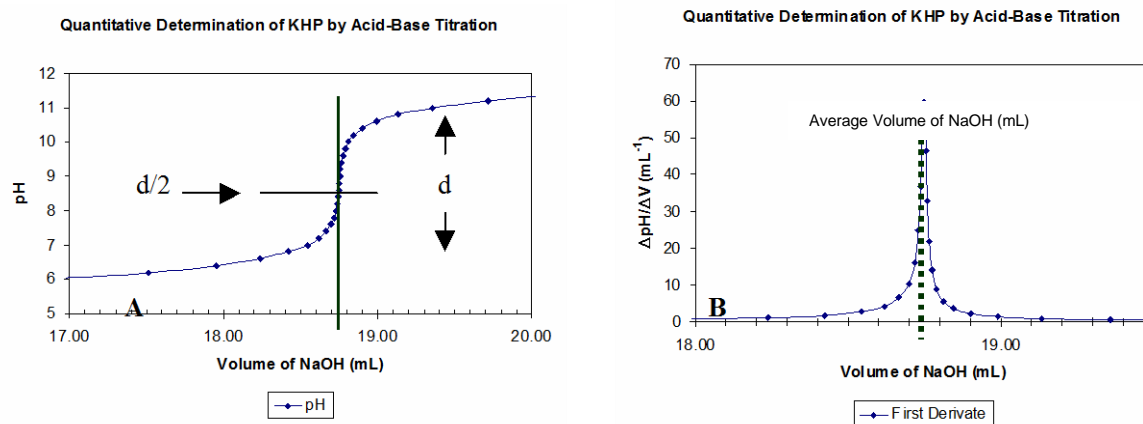


Figure 1: Determination of the equivalence volume for an acid-base titration. A: Plot of pH vs. volume of titrant. The point at half height of the sigmoid (inflection point) corresponds to the equivalence volume of titrant. B: First derivative plot. The maximum value corresponds to the equivalence volume of titrant.

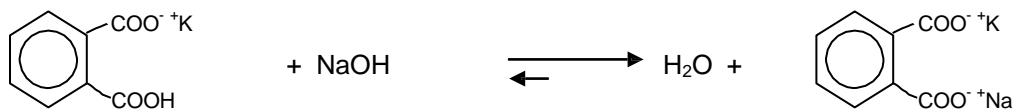
Figure 2 is a screenshot of a Microsoft Excel spreadsheet titled "KHP Figures". The spreadsheet contains the following data:

Data							
Unknown	Final Point	KHP Std.	FW: KHP	Ratio	Volume	NaOH	
Mass (g)	(mL)	% Purity	(g/mol)	(mol/mol)	KHP (mL)	(M)	
0.849	18.75	99.99	204.22	1/1	50	0.11428	
Titration Data							
Vol. Titrant	pH	First Derivate	Formula				
NaOH (mL)		$\Delta\text{pH}/\Delta\text{V}$					
0.00	3.4	0	$=(\text{C13}-\text{C12})/(\text{B13}-\text{B12})$				
0.24	3.4	0.67372804					
0.53	3.6	0.50287371					
0.93	3.8	0.3547316					
1.50	4.0	0.24831782					
2.30	4.2	0.17811325					
3.42	4.4	0.13413729					

Figure 2: Spreadsheet used to determine the equivalence volume in Figure 1. Note that you must be consistent in the units and significant figures of your data.

This experiment will focus on the titration of a weak acid, potassium acid phthalate (KHP), with a strong base, sodium hydroxide (NaOH). KHP is an ideal **primary standard**, with a high formula weight (204.22 g/mol). For most purposes, the commercial analytical-grade salt can be used to standardize a **secondary**

standard such as NaOH. If water dissociation effects are insignificant, the neutralization of KHP with NaOH can be described as:



The results of the analysis can be affected by the presence of CO_2 in the solution. Dissolved CO_2 forms HCO_3^- , an acid that can be neutralized by the titrant, NaOH; this will produce a positive error in the titration. To prevent this error, the water used to prepare both the titrant and analyte solutions, is boiled for five minutes to remove all the CO_2 .

In this experiment, a series of standard KHP samples are titrated with NaOH in order to determine the concentration of the NaOH solution (standardization). The standardized NaOH will then be used to titrate an unknown KHP sample to determine its percent of purity.

PRELABORATORY EXERCISE

1. What is a primary standard, and what are its characteristics?
2. What is the primary standard used to standardize the NaOH solution?
3. What are the differences between the equivalence and end points in a titration?
4. Why do you need to boil the water in this experiment?
5. A student analyzed an unknown sample of KHP by titrating with NaOH. The NaOH solution was standardized with KHP 99.99% pure. The data obtained are reported in the following table.

Standard Sample #	Mass (g)	NaOH volume (mL)	Unknown Sample #	Mass (g)	NaOH volume (mL)
1	0.7023	26.41	1	0.8324	7.80
2	0.7231	26.89	2	0.8634	8.20
3	0.7525	26.52	3	0.8829	8.50

Determine:

- a. The concentration of the NaOH solution.
- b. The average percent of KHP in the unknown.
- c. The relative deviation of KHP (%) in parts per thousand (ppt).
- d. If the accepted value for the KHP sample is 24.22%, determine the relative error in ppt.

APPARATUS AND MATERIALS

- a. Class A Burets, 50.00 \pm (0.05 mL)
- b. KHP standard 99.98%-100.01% pure (as indicated by the instructor).
- c. Unknown KHP sample
- d. Sodium Hydroxide 50% w/v
- e. Phenolphthalein (indicator)
- f. Orion pH meter
- g. Combination glass electrode with a silver-silver chloride reference electrode

EXPERIMENTAL

- a. Obtain the KHP primary standard and the unknown samples from your instructor.
- b. Dry both the primary standard and the unknown samples in an oven for one hour at 110 °C.
- c. Boil 1L of distilled water in a 1L Florence flask for 5 minutes (use a hot plate) to remove all the CO_2 present.
- d. After boiling, cover the mouth of the flask with a cork stopper covered with Parafilm. You can also use an inverted beaker instead of the cork stopper.

Preparation of the Titrant Solution:

In a 500 mL Florence flask dilute 2.00 mL of 50% w/v NaOH in 330 mL of distilled water (boiled). Mix the solution for two minutes.

Manual Titration: (5 titrations = 3 standards + 2 unknowns)

- Accurately weigh (by difference) **three 0.6500-0.7000g samples** of KHP standard and place each of them into a properly labeled 500 mL Erlenmeyer flask. Cover the mouth of the **three flasks** with Parafilm. **Record all your weighing data.**
- Accurately weigh (by difference) **one 0.7500-0.8000g sample of KHP unknown** into a properly labeled 300 mL Erlenmeyer flask. Cover flask with parafilm. **Record your weighing data.**
- Fill the buret with the titrant NaOH solution.
- To each of the standard and unknown samples, add 50 mL of distilled water (boiled) and five drops of phenolphthalein.
- Titrate both the standard and the unknown samples with the NaOH solution until you observe a light pink color that persists for 15 seconds. Record in your notebook the final volumes of your titrations to the nearest 0.01 mL.

Potentiometric Titration: (1 titration of an unknown)

- Accurately weigh (by difference) **one 0.7500-0.8000 g sample of unknown** in a properly labeled 100 mL beaker. Cover its mouth with Parafilm. **Record all your weighing data.**
- Calibrate the Orion 710 pH meter using pH 7 and pH 10 buffer solutions, as described by your instructor,**
- Titrate potentiometrically the unknown sample with the standardized NaOH solution. Add 1.0 mL increments of NaOH until a change greater than 0.2 pH units per 1.0 mL addition is observed. At this point, use 0.10 mL increments. Record the pH after each addition, and also record the volume at which the color of the indicator changes to pink. HINT: You already did a manual titration, so you have an idea of the endpoint.
- Continue adding titrant until the pH is 12.0

CALCULATIONS**Manual Titration:**

- Calculate the molarity of the NaOH solution (3 different values) using the data from each of the titrations of the standard KHP samples:
 - Moles KHP = (mass KHP)*(%purity/100) / MW KHP = moles NaOH
 - M NaOH = moles NaOH / V NaOH
- Calculate the average molarity of the NaOH solution.
- Determine the percent of purity of the unknown KHP sample, using the NaOH volume at the end point of the titration:
 - Moles NaOH = (V*M)_{NaOH} = moles KHP
 - Mass KHP = moles KHP* MW KHP
 - % KHP = (mass KHP/ mass sample)*100

Potentiometric Titration:

- Determine the equivalence point volume for each of your titrations from the pH vs. titrant volume plot, and from the ($\Delta\text{pH}/\Delta V$) vs. titrant volume plot.
- Using the average NaOH molarity, and the equivalent volume for each titration, calculate the percent KHP on each sample.
- Calculate the average % KHP, using the three values you have already calculated.
- Calculate the relative average deviation (rad) in ppt.
- Using the titration data near the equivalent point, construct a grand plot by plotting Vol. NaOH*[H₃O⁺] vs. Vol. NaOH and estimate the equivalent volume of your titration. Refer to your text for details. Compare your results with those obtained in step a.

- f. Determine the titration errors of your experiment by subtracting the equivalent volume to the end point volume for each of your titrations. Calculate the average error.
- g. From the titration curves, determine the individual and the average values of the equilibrium constant K_a for KHP.
- h. Compare the average K_a value of step g with its expected value (check your textbook), and determine the percent relative error.

QUESTIONS

1. Which are the possible sources of error in your experiment and how can you correct them?
 2. What would happen if you do not boil the water used to prepare your titrant and sample solutions?
 3. Why does the typical acid/base indicator exhibit its color change over a range of about 2 pH units?
 4. Why the standard reagents used in neutralization titrations are generally strong acids and bases rather than weak acids and bases.
 5. Explain in your own words how to calibrate a pH electrode.
 6. Do you think that the titration error of your experiment has a significant effect in your analysis? Justify your answer.
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