

CHEM 334 Quantitative Analysis Laboratory

Determination of a Solid Acid by Volumetric Analysis - Volumetric Titration with Colorimetric Equivalence-Point

Volumetric analysis is a method of quantitative analysis in which the amount of a substance is determined by measurement of the volume of a second substance of known concentration that combines with the first substance in known proportions. A titration is the common practical method of volumetric analysis where a solution of accurately known concentration (the titrant) is gradually added to an analyte until the endpoint. The endpoint is defined as the moment of a chemical titration when the number of moles of analyte are fully neutralized by (or reacted with) the added titrant.

The governing equation for a volumetric titration is shown in equation 1.

$$V_{\text{titrant}}M_{\text{titrant}} = N_{\text{titrant}} = n_{\text{stoichiometry}}N_{\text{analyte}} \quad (1)$$

Where V_{titrant} is the titrant volume used in the titration, C_{titrant} is the titrant concentration, N_{titrant} is the number of moles of titrant, $n_{\text{stoichiometry}}$ is the combining ratio of titrant to analyte based on the stoichiometry of the reaction and N_{analyte} is the number of moles of analyte. If the combining ratio is one, as it is in this experiment, then the number of moles of titrant is equal the number of moles of reactant at the endpoint. Otherwise, there will be some other ratio between the number of moles of titrant and analyte.

Some titrants can be prepared directly, for example, by dissolving an accurately measured quantity of a reactive solute in an accurately measured volume of solution. An aqueous solution of sodium hydroxide is commonly used as a titrant for the determination of acids. However, sodium hydroxide is not suitable for use alone as a titrant. As solid sodium hydroxide contains a significant and variable amount of water, it is not possible to prepare a solution with an accurately known concentration of it. In practice, a solution of sodium hydroxide is prepared with a concentration approximately known and the titrant itself is calibrated against a suitable so-called "primary standard" so that the exact concentration can be determined, that is, it is "standardized."

The potassium hydrogen phthalate (KHP) is a suitable primary standard because it is stable as a solid and in solution, it is soluble in water, it is not hygroscopic, it is easily dried and its molecular mass (approximately 200 g mol^{-1}) results in convenient and accurately determined masses of the substance for making solutions. Phthalic acid is a diprotic acid from which KHP is easily prepared by neutralization of one ionizable proton by potassium hydroxide as seen in Figure 1. KHP is also readily available commercially.

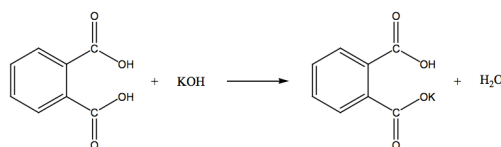


Figure 1. The reaction between phthalic acid and potassium hydroxide to yield potassium hydrogen phthalate (KHP) and water.

The reaction between KHP and sodium hydroxide is shown in Figure 2. From this reaction it can be seen that the combining ratio between KHP and sodium hydroxide is one.

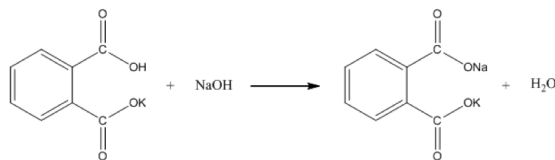


Figure 2. The reaction between potassium hydrogen phthalate and sodium hydroxide to yield sodium potassium phthalate and water.

Titration is the process of adding one solution from a buret (the titrant) to another solution in a flask (the analyte) until all of the substance in the flask has reacted.

In this experiment a solution of sodium hydroxide with an approximate concentration will be prepared. The solution will be standardized, that is, its concentration will be accurately determined by titration against a suitable primary standard (pure KHP). Then, the standardized solution will be used to determine the concentration of KHP present in a mixture of KHP and inert substances. The determination will depend on the volume of sodium hydroxide solution that reacts with the solid acid and the acid-base indicator phenolphthalein will be used to provide a visual indication of the endpoint.

Procedures

Preparation of the Sodium Hydroxide Solution. Prepare 500 mL of a solution that is approximately 0.1 M in sodium hydroxide. Prepare this solution directly in a clean **but not necessarily dry** 500 mL colorless propylene bottle and store the resulting solution in it. Use either solid sodium hydroxide (weighed using a top loading balance only) or from 1 M sodium hydroxide solution. It is sufficient to fill the bottle with water to the top of the cylindrical portion and not necessary to use more accurate volumetric measures. (Explain why.)

Preparation of the Known KHP Standard: Dry approximately 2.0 g of pure KHP to constant weight as follows:

Weigh a clean and dry weighing bottle and its cap accurately. Place the bottle and its cap (separated) in a 110°C oven for fifteen minutes. Remove them from the oven and recap the bottle immediately. After they return to room temperature, weigh the combination. Repeat this process until successive weights agree to 1%. This process is called "drying to a constant weight."

Add approximately 2.0 g of KHP to the bottle and dry to a constant weight. Keep this bottle of dried KHP capped except when necessary to withdraw samples.

Standardization of the Sodium Hydroxide Solution: The sodium hydroxide solution is standardized, that is, its concentration is accurately determined, by titrating an accurately known quantity of solid, dry KHP as follows.

Rinse a buret three times with a few milliliters of the sodium hydroxide solution. Drain the solution through the stopcock and during the last rinse so that all bubbles are eliminated from the tip piece. Fill the buret to the zero mark with the solution. Record the initial solution level to the nearest 0.01 mL.

Add an accurately known sample (0.3-0.4 g) of pure, dry KHP to a convenient titration vessel. Use a 125 mL Erlenmeyer flask. Dissolve the KHP in approximately 20 mL of water and add a few drops of phenolphthalein indicator (10 g L⁻¹ in ethanol) solution. Place the flask on a clean sheet of white paper. Swirl the solution by hand vigorously but gently enough to prevent splashing of the solution.

The actual titration is performed by dispensing titrant from the buret and observing the solution in the flask. The solution will turn pink for a moment as the titrant is dispersed. The endpoint is defined by the first permanent appearance of a pink tint to

the solution. This titration is very sensitive - it is possible to pinpoint the end point of a phenolphthalein titration to a single drop of titrant. The volume of titrant used is measured and reported to the nearest 0.05 mL.

Repeat this process to obtain three standardization determinations.

On a practical note, a titration can be slow to perform. There is a tendency to add titrant very slowly to prevent overshooting the endpoint and this results in a lengthy process. The time to completion can be shortened significantly if the volume of titrant required is known then most of the required volume can be added quickly and the final approach to the endpoint can be made slowly. The entire process can be expedited by first performing a so-called "quick and dirty" titration where the titrant is added quickly (from one to several milliliters at a time) knowing that the endpoint will be "over-shot" but recognizing that the appropriate volume will be estimated and subsequent titrations can be performed relatively quickly.

Determination of the Unknown KHP Sample: Perform a titration on an unknown sample without drying the sample and with performing a "quick and dirty" titration before performing the accurate titration. Recognize and take into account that the required titrant volume will be smaller for a corresponding amount of unknown because the unknown is not pure KHP.

Perform a total of three determinations on separate accurately weighed unknown samples.

Results

Report on the moisture content of the stock KHP including the uncertainty of this measurement.

Report on your results and calculations for the standardization of the sodium hydroxide solution. Clearly report your determination of the concentration of sodium hydroxide in this solution together with the 95% confidence interval of the concentration. Include a suitable error analysis for this material.

Report on your results and calculations for the determination of the concentration of KHP in your unknown sample. Clearly report the concentration in both wt% and in PPM together with the 95% confidence interval of the concentration appropriate for each of the units. Include a suitable error analysis for this material.

Discussion

The amount of water used to dissolve the analyte in this titration is not very critical. Discuss the basis for this.

Also, discuss the basis for the choice of phenolphthalein as an indicator especially since its pKa is 9.3.

Take this opportunity to discuss briefly the strengths and weaknesses of alternate indicators and of alternate endpoint indication methods.

References

- Harris, D.C., "Quantitative Chemical Analysis" (2007) 7th edition, Freeman & Co., NY, see especially "titrations."
- *Titration*, Wikipedia. <http://en.wikipedia.org/wiki/Titration> (accessed Feb 2011).