

THE STANDARDIZATION OF NaOH and KHP ASSAY

A Weak Acid/Strong Base Titration

For this experiment:

- Prepare your lab notebook with a purpose and procedure summary. Also, calculate how much KHP is required for 5 titrations (see the first problem on the prelab). It may also be helpful to prepare a data table, such as the table on the Data Report Sheet. You must get these pages initialed by a lab instructor, with your prelab.
- Complete the prelab and get it stamped by the lab instructor **before** you begin to work on the experiment.
- Titrate your solutions to a **pale pink**. No more magenta solutions!
- Perform 4 titrations and determine the mean Normality of NaOH, the standard deviation, and the RSD for your data. **Your values must have an RSD \leq 5 ppt for this experiment.**
- Enter your mean N_{NaOH} on the spreadsheet at the Instructor station. Complete the data report sheet at the end of the packet. No stamp is needed.

Turn in only the Data Report Sheet, your Notebook Sheets, and the Stamped Prelab!!

You will determine the exact normality of an NaOH solution by standardizing the NaOH against a primary standard (KHP). This NaOH solution will be used in later experiments.

Introduction and Method

In this experiment you will determine the concentration of a sodium hydroxide solution to a high degree of accuracy. This process is called **standardization** and the resulting solution is a **standard solution**. That is, a standard solution is one having an accurately known concentration.

In order to determine the concentration of the sodium hydroxide solution, one must have an especially pure acid so that an accurately measured amount of acid can be weighed out on the analytical balance. The weight of this acid is the starting point for all subsequent calculations and it is therefore called the **primary standard**.

In general, a primary standard is any especially pure chemical that can be used as the starting point to quantify an analysis. Few chemicals are pure enough and stable enough to be used as primary standards. For example, solid sodium hydroxide cannot be used as a primary standard because it absorbs atmospheric moisture and carbon dioxide during storage and also during a weighing operation. A primary standard should have the following qualities:

- a. It must be easily prepared, purified and dried.
- b. It must be stable and easily stored.
- c. So it can be weighed in open air, it must **not** be hygroscopic. It must not react with any of the components of air such as carbon dioxide, oxygen or water.
- d. Suitable methods must be available to test it for impurities. Generally, the total impurities must be less than 0.01-0.02%. The exact assay (i.e., the percent purity) must be known.
- e. The reaction for which the primary standard is to be used must be quantitative and must be fast enough that it goes to completion in a reasonable period of time.

With such a long list of requirements, it is understandable that few substances can be used as primary standards.

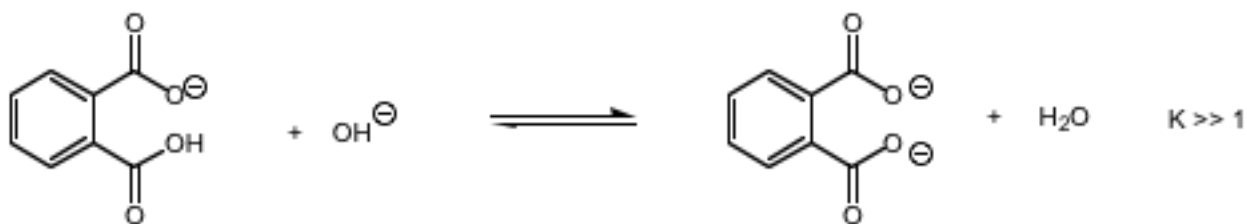
To determine the concentration of a sodium hydroxide solution through a titration, the primary standard must be an acid. In the present experiment, potassium hydrogen phthalate (KHP = $\text{KC}_8\text{H}_5\text{O}_4$) will be used.



Phthalic Acid

Potassium Hydrogen Phthalate (KHP)

The net ionic equation for the titration is:



Since one mole of KHP reacts with one mole of OH^- ions, the equivalent weight is equal to the gram formula weight of KHP (204.22 g/mol).

Sources of Error

- Beginning students in quantitative analysis are sometimes surprised how careful one must be in order to obtain accuracy within a few parts per thousand. Apparatus used must be scrupulously clean. There must be absolutely no loss of material through spillage, splashing or splattering.
- Reading errors. It is easy to read the balance or the buret wrong. Check each reading carefully.
- Your buret must run clean. Be sure there are no air bubbles under the stopcock of your buret.
- Alkaline solutions absorb carbon dioxide from the atmosphere according to the reaction:



Since hydroxide ion is consumed by this reaction, the concentration of a standard sodium hydroxide solution will be changed. Precautions must be taken to protect the standard alkali solution from the carbon dioxide that is always present in the atmosphere. During titration the sodium hydroxide in the buret is exposed to the air; therefore the buret should not be prepared for use until it is needed, and fresh sodium hydroxide should be added if it has stood in the buret for more than about 20 minutes. **Never take more NaOH from the carboy than is needed for ONE titration!** Take only as much NaOH as needed to fill or refill your buret. Tap water and even deionized water may contain dissolved carbon dioxide. To remove the CO_2 , water may be boiled for about three minutes.

- One of the most common causes of poor grades in the quantitative analysis laboratory is arithmetic error in the calculations.

Standardization of 0.1 N Sodium Hydroxide Solution

Dry primary standard potassium hydrogen phthalate, KHP, (a.k.a., potassium biphthalate, a.k.a., potassium acid phthalate) at 110°C for two hours. *This has been done for you! You will not need to dry the KHP before you do the experiment. The technique information remains for your learning pleasure.*

Technique tip for drying and weighing samples.

Place your sample in a weighing bottle and put the weighing bottle, sample and lid into a beaker. Write your name on a small piece of paper and place it in the beaker with your sample. Place a watch glass over the top of the beaker so dirt will not fall into the sample and put the whole thing in the oven. When you remove the beaker and sample (use gloves!), place the sample with cap into a desiccator with dry desiccant to cool, ~1hr. Be careful not to contaminate your sample. The desiccator should have a light coating of grease or petroleum jelly on contact surface with the lid to keep from having air exchange.

Weighing **by difference** involves weighing the weighing bottle, sample, and cap on the Analytical balance, then dispensing a small amount of sample by carefully pouring some sample from the weighing bottle into a second container. Put the lid back on and reweigh the sample and container. The difference between these two masses is the amount of sample transferred to the flask or beaker. You should handle the sample (weighing) bottle and lid only with kim wipes (or tongs) to avoid fingerprints, which can affect your masses.

Weigh out four samples of KHP (**to 0.1 mg by difference**) into four 250-mL Erlenmeyer flasks. You calculated the approximate mass in your prelab. Dissolve each sample in about 50 mL of distilled water before you titrate the sample. Add five drops of phenolphthalein indicator and titrate with constant swirling to the first appearance of a permanent pink color (see Notes 1 – 3). Read your buret to the nearest 0.01 mL.

Calculate the normality of the sodium hydroxide solution from each titration, and determine the mean, standard deviation and the RSD. Report your results on the form provided.

If you feel that one trial is errant, you may apply the Q-test to any divergent results (see Note 4). Remember: a data point must fail both the Q-Test and the 5 ppth test to be rejected. If you discard any data on the basis of the Q-test and 5 ppth test, show these calculations on the back of your report and **circle** the **rejected data**. The normality must be reported with the proper number of significant figures (ppth).

Enter your data into the spreadsheet on the computer in the Laboratory. It is to your advantage to always do the calculations before cleaning up and leaving.

NOTES

Note 1:

The end point is the faintest possible pink color. Place your Erlenmeyer flask on a sheet of white paper to assist you in seeing this faint pink color. If you are not sure whether you have reached the end point or not, record the volume of sodium hydroxide delivered and then add another half drop of titrant. Rinse off any NaOH from the buret tip (with a jet of distilled water from the wash bottle) into the Erlenmeyer flask after each addition of NaOH. If an easily perceptible or bright pink color forms, take the preceding volume for the end point. Repeat this procedure until the endpoint is reached.

The pink color must be permanent for at least 15 seconds. On longer standing, the color may fade and disappear. It is therefore **poor** practice to try to match the color of the second and third titrations with the first titration. One must watch for the **change** in color.

Note 2:

Many times, a "mixed indicator" solution is be used because of its more intense color change. For example, a mixed indicator prepared with two parts of phenolphthalein and one part of methylene green (a green dye) will have the following color change:

<u>pH</u>	<u>Phenolphthalein</u>	<u>Mixed Indicator</u>
8.0	Colorless	Greenish-blue
8.8	Pale pink	Greenish-blue
8.9	Pale pink	Pale blue-gray
9.0	Pink	Violet
9.8	Red-violet	Deep violet

Note 3:

An end point is a color change that indicates when the right amount of titrant is added. The end point is observable. The equivalence point is when the stoichiometric amount of titrant is added to the analyte. In an acid base titration, it is when an equal number of moles of H^+ and OH^- react.

Note 4:

The Q-test must be applied with caution. For example, consider the following set of normalities: 0.1006, 0.1006, 0.1006, 0.1008

Blind application of the Q-test would reject the value 0.1008. However, it differs from the other three values by only two parts per thousand, and in fact is well within the limits of experimental error expected in this titration. There is therefore no basis for rejecting the value 0.1008. In the present case, if the **range** is less than five parts per thousand the suspected value should be retained. (Refer to the Statistic Review Sheet for a more complete discussion of the Q-test and the 5 ppt test.)

APPENDIX

Concentration Units – Normality versus Molarity. Most titration calculations can be carried out using either concentration units, N or M. Remember that **normality** is the number of **equivalents per liter** of solution, where an equivalent is the number of active units per mole of compound. Active units can be H^+ or OH^- for acid/base reactions or electrons for redox reactions.

Example: A 1.5 M H_2SO_4 solution is 3.0 Normal, because there are 2 equivalents of H^+ in every mole of H_2SO_4 .

$$\frac{1.5 \text{ mol } H_2SO_4}{L} * \frac{2 \text{ eq.}}{\text{mol } H_2SO_4} = \frac{3.0 \text{ eq}}{L} = 3.0 \text{ N}$$

Equivalent Weight- the equivalent weight of a compound is the mass of compound that can supply one mole of active units (H^+ , OH^- , e^- 's).

Example: Determine the equivalent weight of barium hydroxide. The formula $Ba(OH)_2$ has a mass of 171.35 g/mol. Since barium hydroxide has 2 equivalents of OH^- per mole, the equivalent weight is 1/2 the molecular weight.

$$\frac{171.35 \text{ g}}{\text{mol}} \times \frac{1 \text{ mol } Ba(OH)_2}{2 \text{ eq } OH^-} = \frac{85.675 \text{ g}}{\text{eq}}$$

SAMPLE CALCULATIONS

Weak Acid — Strong Base Titrations

The equivalence point of the titration occurs when the equivalents of base added exactly equals the equivalents of acid in the flask **or** when moles of base units added exactly equals the moles of acid units in the flask.

$$\# \text{. Equiv. base} = (\text{mL base})(1L/1000 \text{ mL})(N \text{ base})$$

The usefulness of normality in volumetric analysis is demonstrated with following:

$$\text{at the equivalence point} \quad N_{\text{Acid}}V_{\text{Acid}} = N_{\text{Base}}V_{\text{Base}}$$

To calculate the number of equivalents contained in a known acid sample, one needs the sample mass, its purity, and its equivalent weight. The purity factor is simply the % in fractional form.

$$\text{eq acid} = \frac{\text{sample weight(g)} \times \text{purity factor}}{\text{equiv. wt.(g/eq.)}} \quad \text{or in more familiar form}$$

$$\text{path:} \quad \text{g sample} \rightarrow \text{g acid} \rightarrow \text{eq. acid}$$

$$\text{equiv. acid} = \text{g sample} \times \frac{\text{g acid}}{100 \text{ g sample}} \times \frac{\text{eq acid}}{\text{g acid}}$$

Example: Determine the equivalents of acid in a 0.4567 g sample which is 92.15% pure citric acid, a triprotic organic acid, $C_6H_8O_7$.

Because citric acid is triprotic (3 H^+ /molecule), the Equivalent weight = $MW/3$

$$\text{eq acid} = 0.4567 \text{ g sample} \times \frac{92.15 \text{ g acid}}{100 \text{ g sample}} \times \frac{1 \text{ eq acid}}{64.05 \text{ g acid}} = 0.006571 \text{ eq. acid}$$

Example: Calculate the weight of primary standard potassium hydrogen phthalate (assay = 99.95%) that would be required to standardize a 0.1 N NaOH solution, assuming a 40 mL titration.

PATH: L NaOH \rightarrow mol NaOH \rightarrow mol KHP \rightarrow g KHP \rightarrow g sample

Note that 1 equiv = 1 mol for both KHP and NaOH so $N = M$ and molecular weight = equivalent weight.

$$0.040 \text{ L} \times \frac{0.1 \text{ eq NaOH}}{\text{L}} \times \frac{1 \text{ eq KHP}}{1 \text{ eq NaOH}} \times \frac{204.23 \text{ g KHP}}{\text{equiv KHP}} \times \frac{100 \text{ g sample}}{99.95 \text{ g KHP}} = 0.8 \text{ g sample}$$

Therefore, a sample weight between 0.78 gram (which would require a 38 mL titration) and 0.86 gram (which would require a 42 mL titration) would be reasonable. The samples should be weighed accurately to 0.1 mg ($\pm 0.0001\text{g}$).

Example: An 0.8167 gram sample of primary standard KHP (assay = 99.95%) required 38.25 mL of NaOH to neutralize. Calculate the molarity of the NaOH solution.

PATH: g sample \rightarrow g KHP \rightarrow mol KHP \rightarrow mol NaOH \rightarrow M NaOH

$$0.8167 \text{ g sample} \times \frac{99.95 \text{ g KHP}}{100 \text{ g sample}} \times \frac{1 \text{ mol KHP}}{204.22 \text{ g KHP}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol KHP}} \times \frac{1}{0.03825 \text{ L}} = 0.1040 \text{ M NaOH}$$

Example: A 1.7734 gram sample of KHP required 40.11 mL of 0.1036 N for titration. Calculate the assay of the KHP and report with a relative error of 1 part per 1000.

$$0.04011 \text{ L} \times \frac{0.1036 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol KHP}}{1 \text{ mol NaOH}} \times \frac{204.22 \text{ g KHP}}{1 \text{ mol KHP}} \times \frac{1}{1.7734 \text{ g sample}} \times 100\% \\ = 47.8548\% = 47.85\% \pm 0.05\% \text{ (ppth precision)}$$

Example: A 0.8676 gram sample of a pure organic acid required 38.69 mL of 0.1042 N NaOH for equivalence. Calculate the equivalent weight of the acid, and report with a relative error of 1 part per 1000.

$$\text{MW} = 0.8676 \text{ g acid} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol acid}} \times \frac{1 \text{ L}}{0.1042 \text{ mol NaOH}} \times \frac{1}{0.03869 \text{ L}} = \frac{215.2 \text{ g}}{\text{mol}}$$

Name _____

NaOH Carboy ID _____

Trial	1	2	3	4	5 (if needed)
Weight KHP (g)					
Volume NaOH (mL)					
NaOH Normality					
Average Normality					
Standard deviation		Class Normality			
RSD		ppth difference between your data and class data			

NOTE: Report all Normality's to part per thousand precision

If a sample is rejected by the Q-test and the 5 ppth test, circle the data for that sample, and put the Q-test and 5 ppth calculations on the back of this report form. Make another measurement to replace the rejected value and record it into the extra spot on your report form.

Sample Calculation for Normality of NaOH:

Additional space for Calculations (Q-test, 5 ppth test)

Name _____

Using the equations attached to the experiment and all of your knowledge about reactions and statistics answer the following questions.

1. Calculate the approximate weight of KHP required so that about 40 mL of 0.1 N sodium hydroxide will be used in a titration. (E.W. KHP= 204.23 g/equiv.)

mass =

2. Calculate the molarity of a solution of monoprotic KHP prepared by mixing a 0.6237 g in 50.0 mL of water. (E.W. KHP= 204.23 g/equiv.)

M =

3. A 0.6237 g sample of KHP with a purity of 99.99% is titrated with 42.34 mL of NaOH solution. From the data given, calculate the normality of base. Round your answer to the appropriate number of significant figures based upon a precision of 1 ppth.

N =

– Over –

4. Four values of the normality for a NaOH solution were found to be 0.09987 N, 0.09980 N, 0.09882 N and 0.09981 N. Round all values to ppth precision, and check to see if all values should be retained, using the Q test and the 5 ppth test. Report all retained values and calculate the mean, standard deviation and RSD.

Trial	N NaOH		
1		Mean:	
2		Standard Deviation:	
3		RSD (ppth):	
4			