

Chemistry 111 Laboratory
Experiment 8:
Stoichiometry in Solution – Standardization of Sodium Hydroxide

Opening Comments

This is a skill-building experiment, in which you will have to work carefully and use equipment skillfully in order to achieve good results. Learning good titration technique will be helpful in subsequent chemistry labs, not only as a specific skill, but also as it illustrates the excellent results that can be achieved if sound technique is employed. Students should work individually on this experiment: that is, each of you will be carrying out your own titration.

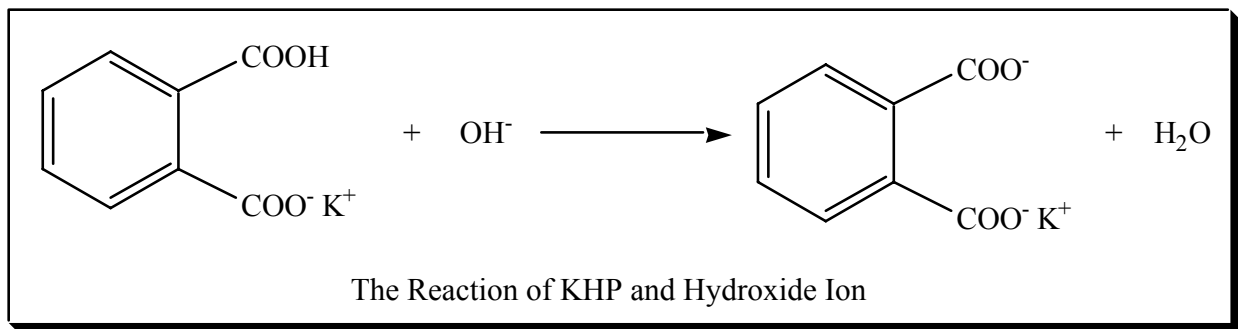
Standardization

Many analytical procedures involve comparison of an unknown with a **standard**. A standard is usually a solution whose composition (concentration) is known very precisely (and accurately!). Unfortunately, NaOH is not a suitable **primary standard**. Solid NaOH is highly hygroscopic (it absorbs water from the air) and thus it cannot be accurately weighed. It also absorbs carbon dioxide from the air, forming sodium carbonate and thereby reducing the amount of sodium hydroxide present. This means that a NaOH solution of known molarity cannot be directly prepared without resorting to an air-and-water-free environment. We can only prepare a solution of NaOH that has the approximate concentration we will need.

In cases like this we need to use an acid as the **primary standard** to determine the exact concentration of the NaOH solution. The primary standard we will use is potassium hydrogen phthalate ($\text{KC}_8\text{H}_5\text{O}_4$, often abbreviated KHP). It is available as a pure, stable, crystalline solid that can be accurately weighed. A KHP sample of known mass (and, therefore, known moles) can be titrated with the NaOH solution to determine very precisely the concentration of the NaOH. This procedure is called **standardizing** the NaOH solution. Once this concentration is determined, the NaOH solution can serve as a standard for further work.

Standardization of Base Using KHP

The amount of the base (NaOH) in a solution can be determined by measuring very accurately the amount of solution required to react with a known amount of acid (KHP). One mole of KHP contains one mole of H^+ that can react with one mole of sodium hydroxide, which contains one mole of OH^- . The net ionic reaction for this weak acid-strong base reaction is provided on the next page. Notice that early in a titration of KHP with OH^- , not much OH^- has been added, so it is the limiting reagent and KHP is left over (*the solution is acidic*). At the equivalence point stoichiometric amounts of KHP and OH^- have been mixed. The product KP^- is a weak base (*the solution is basic*). Just past the equivalence point, KHP is limiting, and so OH^- is left over (*the solution is basic*). The point at which equivalent amounts have been mixed is determined using an indicator that changes color as the solution changes from *acidic* to *basic*. Phenolphthalein is the most commonly used indicator (and the one we will use in this experiment), although many other indicators would also work for this titration.



Accuracy and Precision of Measurements

This week you will make two sorts of measurements. Using a very *precise* balance, you will *accurately* weigh out specific amounts of solid KHP. All weighings should be done to ± 0.0001 g, the limit of our analytical balances. Using a somewhat less precise *buret*, you will accurately measure the volume of your NaOH solution required to react with your KHP. The volume of liquid in a buret should be recorded to ± 0.01 mL, by estimating the value between the marks.

The *precision* with which you measure is critical, and relates to the number of digits you record in your laboratory notebook. For example, when measuring volumes using a buret, you should record volumes with two places to the right of the decimal point, for example, 12.01 mL (12.0 mL would not be *precise* enough). In order for this to be valid, though, you must interpolate (estimate your position between the buret gradations) well enough that your estimate of the last number is off by ± 1 digit, at most. In other words, in this experiment, you need to be able to reliably differentiate between 12.04 and 12.01 mL. ($12.04 \pm .01$ needs to be reproducibly distinguishable from 12.01 ± 0.01 !)

The *accuracy* with which you measure is also critical and has to do with how close the value you report is to the actual value. For example, if the amount really is 12.01 mL, but you have misread your buret and write down 12.21 mL instead, your very precise measurement is useless, because it is not accurate.

When several determinations are made (as you will do here), the overall precision is related to how consistent the data are. For example, if you do three titrations and from them calculate the three molarities 0.1020 M, 0.1022 M, and 0.1018 M, the precision of your work is very high (approximately $\pm 0.2\%$). In this experiment you will quantify your precision so that it can be compared with other people's work. Don't worry if it takes several tries to get a good set of titrations - practice yields proficiency!

Because the objective of our experiment is to make the concentration of our sodium hydroxide solution accurately and precisely known, great care must be taken not to contaminate it. Keep it tightly capped when not in use. Do not allow droplets of solution to evaporate around the mouth of the storage container, or carbon dioxide to enter and react with the solution.

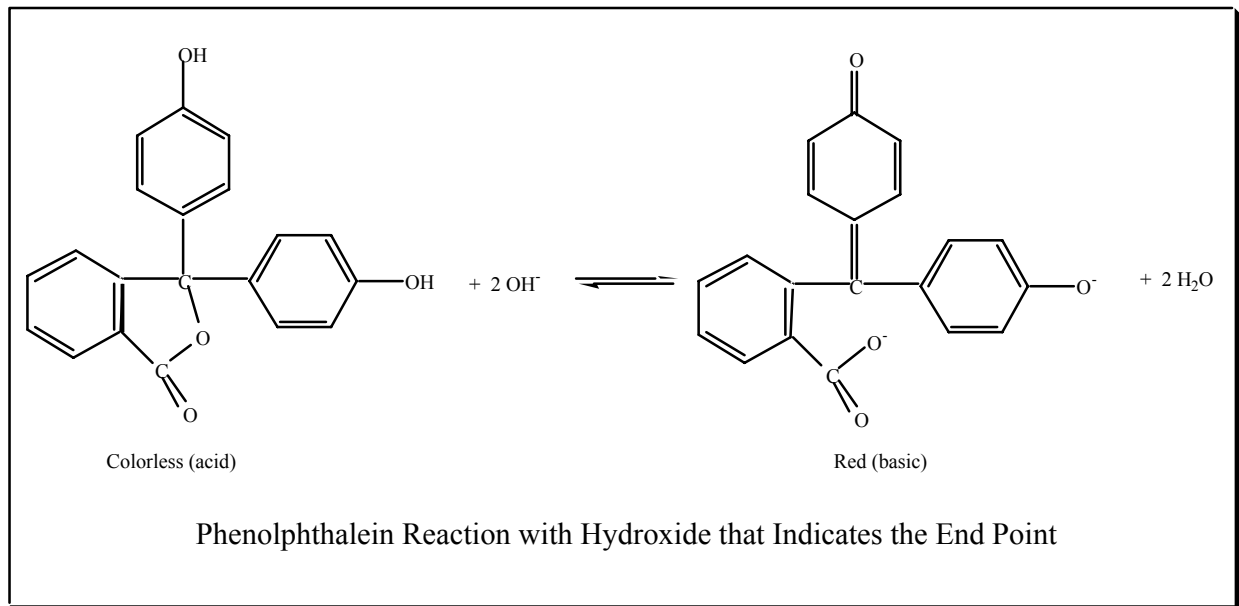
Colorimetric Titration

The method you will use to determine the molarity of your NaOH solution is called a *colorimetric titration*. The basic idea in colorimetric titration is to put one solution (in this case your NaOH solution) into a buret and add it slowly to another (in this case your KHP dissolved in water, containing an indicator dye) until a sudden color change occurs. The buret is then read and a calculation done to determine exactly how much solution was used. This point, when the indicator dye changes color, is called the *end point*.

The color change you will observe is due to the indicating dye undergoing a sudden chemical reaction. In this experiment we will use an acid-base indicator called phenolphthalein. This substance has the interesting property of changing color as the hydrogen ion concentration changes. Phenolphthalein is colorless in acidic or neutral solutions and pink in basic ones (see the reaction below).

In this titration, as the point approaches at which a stoichiometric amount of NaOH will have been added to the KHP, the pH changes suddenly from acidic to basic, the phenolphthalein reacts, and the solution turns from colorless to pink.

Indicator dyes are common in nature, particularly in flowers and fruits. The apple that is green (and sour: too acidic) when unripe and red when ripe (not so sour: less acidic) is a good example. The change in acidity as the fruit ripens triggers a color change in an indicator system, letting the world know that the end point (edible point?) has been reached.

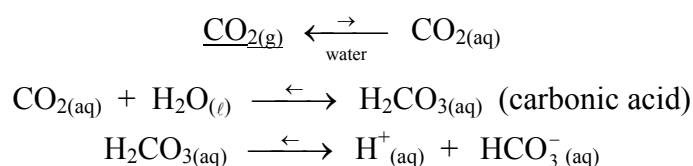


End Points and Equivalence Points

The point (measured in milliliters of solution added) in a titration when the amount of base added is precisely equal to the amount of acid initially present is the *equivalence point*. In a titration, the equivalence point is only approximated by the end point (the point where the color change occurs). Realize that these two points are not precisely the same. In fact, if you used the wrong indicator dye, your measurement could be very inaccurate, no matter how precise you are. In this experiment the end point is within about 0.001 mL of the equivalence point.

A Few Important Words About the “Neutrality” of Water

While we have been generally led to believe that water is neutral, and has a pH of 7, this is only true of very *pure* water, and you’ll rarely find water that lives up to this expectation! The main culprits changing the pH of water are gaseous acids, the most prevalent of which is carbon dioxide. Carbon dioxide is present at a low concentration in the atmosphere, but it slowly dissolves *in* water, and then readily reacts *with* water to form carbonic acid, which loses a proton and thereby lowers the pH:



Happily for us, the first step in this process is sluggish (in both directions – or else our soft drinks would go flat in seconds!), and titrations can be carried out in air without undue interference from carbon dioxide. However, it is critical that we not use water that has carbon dioxide already dissolved in it when we carry out a titration! The water-deionization system at Macalester is also a de-gassification system – so the water that emerges from the DI water taps in our labs is free of both dissolved carbon dioxide and carbonic acid. However, DI water won’t stay that way indefinitely – as it spends time in contact with air, it absorbs carbon dioxide and becomes acidic. A week is plenty of time for this to happen: and you can bet that it has happened to the water that’s been kicking around in your squirt bottle since last week! So, in order to get good results in this lab, it is critical that you avoid using any “old” DI water. First, empty your squirt bottle, rinsing and then filling it with fresh DI water. Second, use DI water directly from the tap to dissolve your samples for this lab. Paying attention to this will pay dividends in the accuracy of your result!

Procedure

Note: A lot of people obsess about getting the perfect color in a titration, and think that not only demonstrates their prowess but also guarantees good results. Alas, good color vision isn't really a big help in titration: rather, good technique, doing such mundane things as rinsing down your flask near the endpoint and reading the buret correctly, are far more important to your result.

A. Preparation of the NaOH Solution to be Standardized

A 0.10 M NaOH solution will be provided for you. The solution should be tightly covered when not in use, to avoid evaporation and to exclude acidic gases such as CO₂. Since glass will react with strong bases (and slowly dissolve!), NaOH solutions stored for any extended period of time should be kept in *plastic* bottles, and you'll see that will be the case with the ones we provide.

B. Preparation of KHP Solutions

Clean your four largest Erlenmeyer flasks (two 250 mL and two 125 mL). The flasks should be clean but need not be perfectly dry (with what **kind** of water should they be wet?) While you are at it, you may also want to clean your two 400 mL and your two 250 mL beakers, as they may also be needed for titrations. In cleaning your glassware, understand that appearance is not nearly so important as neutrality – in other words, if there's some bubble gum stuck to the inside of your beaker, you don't really care, so long as it does not act as an acid or a base. Consequently, whatever you do, **don't use soap in cleaning your glassware!** Soap is a base: it will mess up your results! Not only is it hard to wash off, but it is strong enough to change the surface of glass and make it basic as well. So even if you wash off all the soap, the glass that contacted the soap will still act to neutralize some of your base and throw off your results. Dry the *outside* (not the inside!) of each flask (so that you can write on it), and use a Sharpie to mark each flask with a different number.

Dried KHP will be furnished in weighing bottles. You calculated roughly how much you need to use in your Advance Study Assignment: you won't get exactly that amount, especially weighing by difference, but that's fine, so long as you can titrate what you do put in your flask with a single buret (≤ 50 mL) of base. Weigh, by difference, four samples into individual Erlenmeyer flasks. ***Weigh the weighing bottle, not the flask.*** Detailed instructions for weighing by difference appear at the back of these instructions. The mass of each KHP sample can be different, as long as you record each one's mass precisely. The samples are prepared for titration by dissolving each in *roughly* 50 mL of *fresh* deionized water. (DI water that has been sitting around for a long time will have become saturated with carbonic acid, by means of the reaction described up above, and will have a pH of about 5!) Each sample must be completely dissolved before the titration is completed, and preferably before it begins, so add water to all of your flasks right away. Also, to be sure you don't forget it, **add 2 - 4 drops of phenolphthalein to each flask. Without this, your titration efforts will be in vain!** Prepare a wash bottle filled with *fresh* deionized water to wash down the insides of the flask as you near the end point.

C. Preparation of the Buret

This procedure will be discussed and demonstrated in the laboratory. If you spill any base, clean it up immediately, before it ruins your clothes and lab book.

D. Titration -- done four or more times

Before you start each titration, use the equation you derived in your ASA to estimate the volume of titrant that will be needed for the titration you are about to perform. You can add titrant quickly up to within about 3 mL of this, then start adding slowly and working carefully.

Be absolutely certain you know how to correctly read a buret to ± 0.01 mL.

During the titration the flask should be swirled gently (in a smooth circular motion) to insure good mixing. Initially, only a small pink spot will be seen where the titrant enters the solution. It is helpful to place a white sheet of paper below your solution to serve as a background for viewing the pink color. As this pink color persists longer and longer, the rate of addition of titrant should be decreased. The conclusion of a titration should be done using a fractional drop on the buret tip, touching the drop to the wall of the flask, and rinsing it into the solution with your wash bottle. Alternately, the stopcock of the buret may be rapidly rotated through the open position, causing a very small aliquot of titrant to emerge from the buret – the advantage of this approach being that no drop will stick to the buret tip, and less water is needed. This is only important insofar as it reduces the dilution in the intensity of the color change, though. As you get close to the endpoint, the sides of the flask should be rinsed with small portions of water to insure that all the acid and base in the flask are in the main body of solution.

The end point is taken as the first detectable pink color that persists for 20 or more seconds. The pink color will not last indefinitely, because CO_2 from the atmosphere will be absorbed by the solution. When you are very close to the end point, color will spread throughout the solution for a brief period, and then go away. At this point fractional drop additions should be started. Continue until the faintest pink color that persists for 20 seconds or more is seen. The tendency of the solution to absorb CO_2 from the air suggests that the end point should be located as quickly as possible without making errors.

Calculations

Calculate the molarity of your NaOH solution indicated by what you consider to be the best of your first three trials by hand, in your lab notebook. This “sample calculation” should be shown in detail, with careful attention paid to significant digits. If you do not obtain a molarity between 0.09 and 0.11 M, seek help from your instructor or prefect. Once you know how to do the calculations by hand, proceed to the computer lab and set up a spreadsheet to do the others. (Each student should do this *individually* – do not use someone else’s spreadsheet.) For each trial you carried out, calculate the molarity of your base. Then, calculate the average molarity, and the *standard deviation* (in molarity units), over all of your trials. Standard deviation (σ) is an absolute measure of precision, and it is readily calculated with Excel’s STDEV function.

The smaller the standard deviation, the more consistent and reproducible (“precise”) your results are. Divide the standard deviation by the average molarity (use the spreadsheet) to give a unitless measure of the precision of your data known as the *coefficient of variation*, or COV. (This should be familiar from the previous lab, in which you calculated the same ratio to quantify the “constancy” in your K_{eq} values.) For example, if $\sigma = 0.0012$ M and $x = 0.1080$ M,

$$\text{COV} = \frac{\sigma}{\bar{x}} = \frac{0.0012 \text{ M}}{0.1080 \text{ M}} = 0.011 \text{ or } 1.1\%$$

The smaller this ratio, the more consistent your results. In this experiment we are asking you to carry out at least three titrations whose COV is less than 0.8% ($\sigma/x < 0.008$). If your σ/x ratio is greater than 0.008, you will need to carry out additional titrations until three of them agree with each other to within a COV of 0.8%; see your lab instructor or prefect if you need help with your technique!

What to Hand In

Clearly indicate (ideally, in a table) the mass of KHP, initial and final buret readings, and calculated molarity for each trial. Be sure that you have shown detailed calculations (done by hand!) for one of your titrations. Submit a printed copy of your spreadsheet that shows all the raw data in a neat format, and calculates the molarity for each trial. Your spreadsheet should also calculate the average, standard deviation, and coefficient of variation for the three or more trials that combine to give you a COV of less than 0.8%. The trials that you are “using,” which contribute to these statistical values, should be clearly identified, but the calculations and data for *all* of your trials, both good and bad, should appear somewhere in both your lab notebook and spreadsheet. **Be sure to indicate the units of every value, in both your spreadsheet and lab notebook.** When setting up your initial data tables, allow for the possibility that you may have to carry out many titrations: make the rows (rather than the columns) of your table correspond to individual trials, and leave space below the table so that you can expand it if need be.

APPENDIX A: WEIGHING BY DIFFERENCE

Weighing by difference is the most accurate method for quantitatively determining the mass of a solid sample. This procedure involves repeatedly determining the mass of a weighing bottle containing the solid reagent. As the solid to be used is removed to another vessel, the mass of the weighing bottle contents decrease. Upon reweighing, a lower mass is found for the weighing bottle. The difference in the two masses represents the mass of solid reagent transferred to the other vessel - hence the name, "weighing by difference."

How to do it:

You will find weighing bottles (without their caps) sitting in several dessicators in the balance room. They will have been dried in an oven at 120°C for three hours, and then cooled in the dessicators. The dessicators contain a drying agent, and ensure that the water driven out of the solid KHP during the drying process does not return. The dessicators contain a white drying agent, as well as an indicator that is blue when water-free, but which turns pink when exposed to water. If you make the indicator crystals in a dessicator turn pink, you have done a bad thing.

- 1. Bring your *labeled* titration vessels and your lab notebook to the balance room.**
- 2. Open a dessicator and remove a weighing bottle, using a loop of scrap paper.**

This is a bit of a learned motor skill. You can either use the paper as a lasso, and put it around the bottle, or as a mini-glove for your thumb and forefinger. The important thing is to avoid getting fingerprints on the weighing bottles, but also to avoid dropping them! We can't use real gloves, because they build up static charges that make the KHP fly all over the place, as well as significantly impact the balance readings. Close the dessicator.
- 3. Place the weighing bottle on the balance pan, using your loop of scrap paper.**
- 4. Tare out the weighing bottle on the analytical balance.**

You will need to close all of the doors on the analytical balance, and keep anyone from shaking the balance table, in order to have the balance settle down and provide a stable reading in the last decimal place. *Then* you can hit the TARE button. It's important that you tare correctly for this method to work well.
- 5. Remove the weighing bottle from the balance with the paper loop, and *pour* a small amount of solid reagent into one of your titration vessels.**

It is better to transfer too little than too much! If you don't have enough, you'll just have to transfer some more. If you have too much, you will need to start all over. Note that for this experiment you have a lot of leeway: you calculated how much KHP will require 30. mL of titrant to neutralize, but the buret can handle 50 mL of titrant, so you should be OK with up to 1.5 times your calculated mass of KHP. The most reliable means of transferring a controlled amount of solid out of a weighing bottle seems to be rotating it along its long axis while the bottle is tilted as you would to pour out the contents.
- 6. Return the weighing bottle to the balance. If you have not transferred enough KHP, repeat Step 5. If you *have* transferred enough, close the balance doors, wait for the balance reading to stabilize, and record the *exact* mass of KHP transferred.**

Understand that the method you are using here hinges critically on the assumption that all the solid that left the weighing bottle ended up in your titration vessel. This must be rigorously true! If you spill any KHP out of the bottle into anything other than the titration vessel you are working with, you need to start over.
- 7. Repeat Steps 4 - 6 for your other titration vessels.**
- 8. Return the weighing bottle to the dessicator.** Be sure to put the lid on the dessicator.

Name _____

Chemistry 111 Laboratory
Experiment 8:
Stoichiometry in Solution – Standardization of Sodium Hydroxide
Advance Study Assignment

Please answer the following questions on this sheet, before you come to lab.

First, read through the experiment carefully. Then provide a 1-2 sentence synopsis of the objectives of the experiment in the box below.

1. Explain why the volume of water used to dissolve the KHP need not be carefully measured, despite accuracy being crucial in many other aspects of this experiment.

2. Your NaOH solution will be 0.10 M. You would like each titration to use 30 mL (30 ± 10 mL) of base. Calculate the mass of KHP you should be aiming to use in each titration.

3. Devise a formula that will allow you to predict the approximate volume, in mL, of 0.10 M NaOH that will be required to titrate a mass x , in grams, of dry KHP.
4. What type of water should be used throughout this experiment, and why?
5. Read through the instructions for weighing by difference. Identify at least one aspect of this method that makes it possible for it to yield more accurate results in massing small quantities of fine powders than would “normal” weighing. (What potential sources of error does it avoid, relative to other possible techniques?)